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A COURSE OF PRACTICAL CHEMISTRY

BY

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Part I.—ELEMENTARY

EXPERIMENTS ON CHEMICAL CHANGE
PREPARATIONS OF VARIOUS COM-
POUNDS
REACTIONS OF ACIDS, ALKALIS, AND
SALTS

AN ELEMENTARY COURSE OF VOLU-
METRIC ANALYSIS
QUALITATIVE ANALYSIS OF MIXTURES
OF SALTS CONTAINING NOT MORE
THAN A SINGLE METAL IN ANY
ONE GROUP

SECOND EDITION

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PREFACE

THIS book is offered to students and teachers as the first part of what I hope may prove to be a tolerably satisfactory, and fairly systematic, course of Practical Chemistry. It is the first portion of the result of very many attempts, made during twenty-five years, to devise a workable system of teaching in the laboratory.

My experience as a teacher convinces me that qualitative analysis cannot be introduced with any hope of profit at an early stage of a course of practical chemistry. I have, therefore, placed a somewhat extended course of preparations, and of experiments on the reactions of some of the chief classes of inorganic compounds, before the section which deals with the elements of qualitative analysis.

The directions for performing the various experiments are given in considerable detail; because I have always found that superficial directions lead to, and encourage, superficial slipshod work. At the same time, I have endeavoured to lead students to use their reasoning faculties by introducing exercises to be worked out in the laboratory by applying the methods, and the results, of experiments full details for the performance whereof have been given.

In all the experiments I have endeavoured to pay heed to the exigencies of teaching practical chemistry to classes of students, and to students who have not very much time to devote to the study.

The book ought to be used in connection with Lectures and Demonstrations. The first section follows pretty closely the order in which I have attempted, for some years, to develop the subject-matter of elementary chemistry in my own lectures.

All the experiments described in this Part have been tried repeatedly in the laboratory. By the kindness of the Publishers I have been allowed to use the proof-sheets in the laboratory before making the final corrections. I can, therefore, affirm that the experiments are workable.

In *Part II.* I hope to include a more extended series of experiments on the preparation, and reactions, of typical inorganic compounds; a fairly complete course of volumetric analysis; a certain amount of gravimetric analysis; experiments on such subjects as the determinations of equivalent and combining weights; and a course of qualitative analysis.

Part III. will contain a course of gravimetric, and general, quantitative analysis; the preparation, and analysis, of inorganic compounds the manipulation of which requires considerable skill; a certain amount of physico-chemical quantitative work; and, perhaps, the preparation and analysis of typical organic compounds.

M. M. PATTISON MUIR.

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A COURSE OF PRACTICAL CHEMISTRY

PART I

ELEMENTARY

SECTION I

Experiments on chemical and physical changes; mixtures and not-mixtures; elements and compounds; methods of investigating chemical occurrences; preparation, and some properties, of oxygen and hydrogen; typical reactions of oxides; interactions of metals and acids; interactions of metallic oxides and acids, preparations of salts; reactions of acids with salts and with other compounds; characteristic properties of alkalis; interactions of alkalis and salts.

Note I.—Every experiment must be performed carefully, close attention being paid to the directions; for instance, when you are told to ‘*heat gently*,’ this means, use a small Bunsen flame for heating and keep the flame at some distance from the apparatus to be heated.

Note II.—Always read the whole of the directions before beginning an experiment.

Note III.—A list of apparatus and materials required for each lesson is given at the beginning of the lesson. Each lesson will occupy from one and a half to two hours.

Note IV.—In the appendix on MAKING APPARATUS will be found directions for boring holes in corks, bending and fitting glass tubes, and the like.

Another appendix contains various *tables* that will be found useful in laboratory work.

Lists of substances suitable for the various exercises will also be found in an appendix.

LESSON I

CONTRAST OF PROMINENT CHARACTERS OF PHYSICAL AND
CHEMICAL CHANGES

Apparatus and materials required.—Piece of thin iron wire. Emery paper. Six dry test-tubes. Two good corks to fit test-tubes. Piece of glass tubing about $\frac{1}{4}$ inch diameter inside. Rat-tail file, and a cutting file. Taper. Chips of wood. Coarsely powdered sugar. Dry white sand. Dry burnt lime. Salt. Iron filings. Dry ammonium chloride.

It is taken for granted that each student has a set of ordinary apparatus, including such things as test-tubes, basins, beakers, funnels, filter papers, glass rods, and tongs; also that he is provided with the ordinary reagents; and that clamps, retort and filter stands, drying chambers, and the like are at hand.

Experiment I.—*To contrast the effects of heat on iron wire and wood.*

A. Clean, with emery paper, a piece of iron wire a few inches long and about as thick as the line in the margin; and bring the tip of the clean wire into the non-luminous flame of a Bunsen lamp.

The iron wire glows; it emits light.

After a few seconds remove the wire from the flame: the iron is more greyish blue in colour than it was before; but so far as can be judged by looking at the wire it is still iron.

B. Fit a dry test-tube with a softened cork (see appendix on MAKING APPARATUS); then remove the cork and bore a hole through the middle of it lengthwise of a diameter such that a short piece of glass tubing, about 3 mm. (one-eighth of an inch) internal diameter, can be fitted tightly into the hole and pass through the cork. The piece of glass tubing should be about

50 mm. (about 2 inches) long; the ends must be held in a hot flame for a few moments till the edges of the glass melt (see appendix on MAKING APPARATUS). Fill the tube to about one-fourth with small chips of wood, insert the cork with the glass tube fitted into it, and heat the lower end of the tube, gradually raising the temperature (see figure 1).

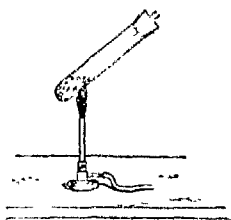


FIG. 1

The wood chars; drops of moisture appear on the sides of the tube; something is given off which smells like burnt wood; and if a lighted taper is brought to the end of the glass tube after the heating has been continued for two or three minutes, the vapours that are issuing from the tube take fire. When the contents of the tube are allowed to cool it is evident to the sight that some of the wood has been changed into something which is very different from the original wood.

A much more profound and more permanent change has been brought about by heating wood than by heating iron wire.

Experiment II.—*To contrast the effects of heat on ammonium chloride (sal ammoniac) and sugar.*

A. Press a little sal ammoniac between filter paper until no wet stain is left on the paper; fill a dry test-tube to about one-eighth with the dry sal ammoniac, and heat the lower end of the tube *very gently* for a few minutes, closing the mouth of the tube loosely with the thumb. You notice that some of the sal ammoniac vaporises, and that the vapour becomes solid again on the colder (upper) part of the tube.

The change of a solid to a vapour by heat, which vapour when cooled changes back to a solid, is called *sublimation*; the solid formed by cooling the vapour is called a *sublimate*.

Remove a little of the sublimate from the tube and compare it with the original sal ammoniac: (1) by noticing the appearances of the two solids; (2) by tasting a *very little* of each; (3) by shaking small portions of each with cold water and noticing how easily both dissolve; (4) by boiling a little of

each with a few drops of a solution of caustic potash (potash lye), and noticing the smell of ammonia (spirits of hartshorn) given off by both.

As far as you can determine by these rough tests the sublimate is the same substance as the salammoniac before heating. The process of heating salammoniac does not seem to have changed that substance into anything else.

B. Heat a few pieces of coarsely powdered sugar in a dry test-tube, raising the temperature very gradually, and heating the tube from the lower end upwards. The sugar chars; steam is produced; there is a smell of something which is not sugar; and the white fumes which come off after the heating has been continued for a few minutes take fire when a lighted taper is brought near the open end of the test-tube.

Sugar is evidently changed, when it is heated, into things which are quite different from sugar; whereas heating salammoniac does not change that substance permanently into anything different from itself.

Experiment III.—To contrast the effect of heat on a mixture of salammoniac and sand with the effect on a mixture of salammoniac and lime.

A. Heat a little dry white sand in a dry test-tube; the sand is not altered in any way that is apparent to the senses.

Now mix, in a mortar, less than quarter of a test-tubeful of salammoniac dried by pressure between filter paper, with about an equal quantity of dry white sand; place the mixture in a dry test-tube and heat the lower end of the tube gently, over a low flame, keeping the mouth of the tube loosely closed with the thumb.

The salammoniac gradually sublimes on to the upper, cooler, part of the tube; and the sand remains in the lower, hot, part of the tube. Remove the sublimate from the tube by the help of a spatula and use the tests mentioned in *Experiment II.*, A, to indicate that the sublimate is salammoniac.

The sand seems to retain its own properties, and the salammoniac to retain its own properties, in the mixture of sand and salammoniac; the experiment does not suggest

the production of any new substance by heating a mixture of these two bodies.

B. Heat a little dry burnt lime in a dry test-tube; no visible change occurs, nor is anything given off that can be smelt. The lime is apparently unchanged. Now mix, in a mortar, less than quarter of a test-tubeful of dry salammuniac with about twice as much dry burnt lime; transfer the mixture to a dry test-tube, place a little dry burnt lime over the mixture, and heat, gradually raising the temperature. After a minute or two the sense of smell tells you that ammonia is being given off from the heated mixture; ~~no~~ sublimate of salammuniac is formed.

This experiment proves that at least one new substance (ammonia) has been formed by heating a mixture of salammuniac and burnt lime. The result of part B of this experiment should be contrasted with that of part A; in the latter chemical change did not occur, in the former something was produced quite different from the substances that reacted to produce it.

Experiment IV.—*To contrast the action of water on salt with the action of diluted sulphuric acid on iron.*

A. To about a test-tubeful of water in a small basin add common salt, a little at a time, and stir with a glass rod; continue to add salt, and to stir, as long as the salt disappears in the water. Then pour off some of the clear liquid from above the undissolved salt into another small basin, and remove the water by placing the basin on a piece of wire gauze and evaporating over a small flame, stirring constantly while the evaporation is proceeding (to prevent spirting). You obtain a white solid substance like common salt; and if you taste a little of this substance you perceive that it is salt.

B. Pour about two test-tubeful of diluted sulphuric acid into a small basin; heat the liquid, and add about one-fifth of a test-tubeful of iron filings; warm for a few minutes until gas comes off freely, then remove the lamp, and when the action has slackened considerably pour the liquid in the basin.

down a glass rod on to a folded *filter paper*¹ that has been moistened with water after being placed in a funnel which is supported in a filter stand (see figure 2), and collect in a basin the liquid which runs through the filter; this liquid is called the *filtrate*.

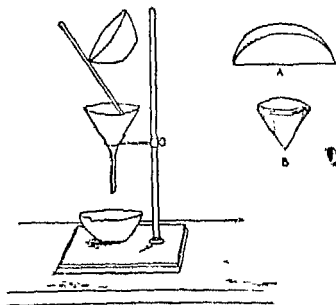


FIG. 2

The filtration is performed in order to get rid of the unchanged iron.

As the filtrate cools a pale greenish solid forms.² A comparison of the appearance of this solid with that of the iron which was put into sulphuric acid shows that the two substances are very different from one another.

The iron has not dissolved unchanged in the sulphuric acid, as the salt dissolved unchanged in water in part A of this experiment; but the iron and the sulphuric acid have reacted to produce a substance which is different from either of them. Chemical change has occurred in one part of this experiment.

The iron has not dissolved unchanged in the sulphuric acid, as the salt dissolved unchanged in water in part A of this experiment; but the iron and the sulphuric acid have reacted to produce a substance which is different from either of them. Chemical change has occurred in one part of this experiment.

Note.—What evidence did part B of *Experiment IV.* give of the production of some substance (or substances) different from iron and sulphuric acid, besides the greenish white solid?

Note.—Quantities of solids are measured by weight; the unit of weight generally used in chemistry is the *gram*. Quantities of liquids are usually measured by volume; the unit of volume generally used in chemistry is the *cubic centimetre*. One cubic centimetre of pure water at 4° C. weighs one gram.

¹ The method of folding a circular filter paper is indicated in A and B, fig. 2.

² Should no solid form in the cold liquid, boil the liquid until its bulk is reduced to about one half, and allow to cool.

LESSON II

CONTRAST OF PROMINENT CHARACTERS OF PHYSICAL AND
CHEMICAL CHANGES—*continued*

Apparatus and materials required.—Coarsely powdered sugar. Coarsely powdered marble. A good cork to fit a test-tube. Piece of glass tubing about $\frac{1}{2}$ inch internal diameter and 6 to 8 inches long. Another piece of glass tubing about 14 to 16 inches long and $\frac{1}{2}$ inch internal diameter. Thin glass jar about 6 to 6 $\frac{1}{2}$ inches tall and 3 to 4 inches diameter. Dry test-tube. Flask about 1 oz. capacity; another 2-oz. flask with a rather long neck, fitted with good cork. Rat-tail file, also cutting file. Beaker about 6 to 7 inches high by 3 to 4 inches diameter; basin to cover mouth of this beaker. Tapers. Lime water.

Experiment I.—*To contrast the action of water on sugar with the action of hydrochloric acid on marble.*

A. Place about half a test-tubeful of powdered sugar in about a test-tubeful of warm water in a small basin, and stir with a glass rod; the sugar gradually disappears. *Has the sugar changed into something which is not sugar—as the iron did when it was dissolved in diluted sulphuric acid in Experiment IV., B., in Lesson I.—or is the sugar present in the water?* To answer this question remove the water by evaporation, and see whether sugar, or something that is not sugar, remains. For this purpose place the basin on a piece of wire gauze, on a tripod, and heat over a very small flame until froth begins to form pretty freely on the surface of the liquid; then remove the basin from the gauze and place it on the top of a beaker in which water is kept boiling, a

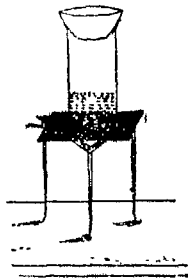


FIG 3

narrow space (for the escape of steam) being left between the rim of the beaker and the basin by slipping a folded piece of paper under the basin (see figure 3).

This device serves to keep the contents of the basin at a constant temperature, nearly that of boiling water; and, there is no risk of the temperature rising high enough to char the sugar (compare *Experiment II., B., Lesson I.*).

This process is called *evaporation on a steam bath*.

Stir the contents of the basin briskly while evaporation is proceeding (the steam is thus allowed to escape more freely and evaporation is hastened), and continue the process until only a white, dry solid is left in the basin. The solid is like sugar to look at, and it has the sweet taste of sugar; moreover, if you heat a little of it in a dry test-tube it chars and smells like burnt sugar (see *Experiment II., B., of Lesson I.*)

The answer which the result of this experiment gives to the question propounded at the beginning of the experiment is: the sugar has, very probably, not been changed into any new substance by dissolving in water; physical change took place, but, so far as the experiment shows, chemical change did not occur.

B. Pour some water on to a little coarsely powdered marble in a test-tube, and then heat the water; the marble is not changed visibly. Now pour a small quantity of hydrochloric acid into the tube. Brisk effervescence occurs; the gas that comes off is colourless, and it extinguishes a lighted taper brought close to the mouth of the tube. Fit a test-tube with a cork carrying a piece of glass tubing bent as shown in figure 4; fill another test-tube to about one-sixth with clear lime water; pour conc. hydrochloric acid which has been diluted with three or four times its bulk of water into the tube fitted with the cork until the tube is about quarter full; slip a few pieces of coarsely powdered marble into the tube containing the acid—inclining the tube, so that the marble slips in gently—at once put in the cork, and let the gas that is produced bubble through the lime water.

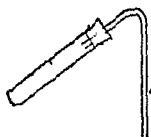


FIG. 4

Describe exactly what you see occurring in the lime water.

You must now find out whether the marble has merely dissolved in the acid, as sugar dissolved in water in part A of this experiment, or whether a new substance has been produced. For this purpose allow the effervescence to proceed for about five minutes, pouring a little more diluted hydrochloric acid on to the marble if the effervescence stops, and then pour the liquid from above any marble that remains into a small basin and set this basin on a piece of wire gauze; bring a *very small* Bunsen flame beneath the gauze, and stir the contents of the basin with a glass rod continuously until the liquid is removed completely and a dry, white solid remains.

The constant stirring during evaporation over the flame is to prevent spitting.

To determine whether the white solid you have obtained by dissolving marble in diluted hydrochloric acid is, or is not, unchanged marble, you must compare the properties of marble with those of the substance you have obtained. You know that marble does not dissolve in water, but that it dissolves slowly with effervescence in diluted hydrochloric acid; shake a little of the white solid with water, and a little with diluted hydrochloric acid, and note the result in each case. Also expose a little marble and a small quantity of the white solid to the air for five or ten minutes, and note any change in the appearances of the two substances.

Experiment I., parts A and B, shows that sugar does not undergo any great change when it dissolves in water, for the sugar is obtained again when the water in which it was dissolved is removed by evaporation; but that marble reacts with diluted hydrochloric acid to produce at least two things different from itself, namely, a colourless gas which puts out a lighted taper and produces a white solid in lime water, and a white solid that dissolves easily in water and becomes wet (deliquesces) in the air.

Experiment II.—To contrast the burning of coal gas with the effect of heat on water.

A. Draw out a piece of glass tubing about 6 mm. wide (about $\frac{1}{4}$ inch) and about 300 mm. (12 inches) long, near one end, cut the

tube at the narrowed part, and hold each end of the tube in the Bunsen flame for a moment or two till the rough edges of the glass are fused smooth; now bend the tube a short distance from the narrowed end, so that when the tube is held vertically the narrow end points upwards, as shown in figure 5. Connect the wider

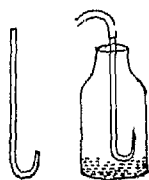


FIG. 5

FIG. 6

end of this tube with the gas supply, by means of caoutchouc tubing; set fire to the gas issuing from the narrowed end of the tube, and turn down the gas until the flame is about 10 to 12 mm. (say about an inch) long. Into a clean, wide-mouthed, thin, glass jar,¹ pour enough clear lime water to completely cover the bottom of the jar, and lower the tube into this jar until the jet of burning gas is about 50 mm. (2 inches) above the lime water (see figure 6). Allow the gas to burn for four or five minutes, then remove the tube, and shake the jar while the mouth of it is covered with the hand or a glass plate; white solid matter forms in the lime water. As the burning gas was odourless, while coal gas has a marked smell, it is evident that the coal gas was changed into some new thing, or things, while it was burning; and this conclusion is supported by the formation of the white solid in the lime water.

But it may be supposed that the substance which produced the white solid in the lime water was contained in the coal gas, and was not produced by burning the gas. To test this hypothesis, clean the jar *thoroughly*, then pour a little clear lime water into it, and allow coal gas to bubble through the lime water for a few minutes; as the lime water remains clear, you conclude that coal gas does not contain anything which produces a solid in lime water, but that something having this property is produced while coal gas is burning.

B. Pour some distilled water into a flask of about 120 c.c. (about 4 oz.) capacity, place the flask on a piece of wire gauze, and heat it until the water boils. Fill a small flask, with a rather long neck, of about 60 c.c. (about 2 oz.) capacity with water; close the flask by a good cork, and hold it in the position

¹ A jar about 160 mm. (6½ inches) tall and 100 mm. (4 inches) diameter is a convenient size.

shown in figure 7 (a test-tube holder may be used to support the flask). Drops of a colourless liquid like water form on the outside of the cold flask and fall into a clean dry basin placed beneath, as shown in the figure. Taste the liquid that collects in the basin; it is evidently water.

The first part (A) of Experiment II. presents

- case of the permanent change of one substance (coal gas) into new substances unlike itself; while the other part (B) of that experiment shows the temporary change of a

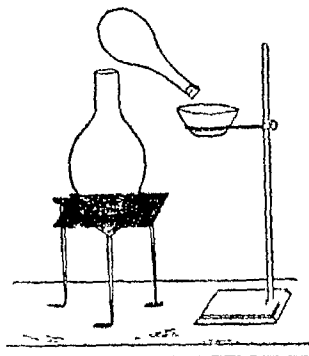


FIG. 7

liquid into a gas (water into steam), followed by the reformation of the original liquid when the gas is cooled. Compare these results with the permanent changes of wood and sugar into new substances when heated (Lesson I., Experiments I., B, and II., B); and with the temporary change of sal ammoniac into a gas by heating the sal ammoniac (Lesson I., Experiment II., A).

LESSON III

CONTRAST OF PHYSICAL AND CHEMICAL CHANGES—*continued*.
MIXTURES AND NOT-MIXTURES

Apparatus and materials required.—A few dry test-tubes. Good cork to fit test-tube. Rat-tail file. Piece of bent glass tubing about 6 inches long used in *Lesson II., Experiment I., B.* Beaker for steam-bath and basin to cover mouth of beaker. Calico. Powdered marble. Sugar. Mercury. Pure iodine. Alcohol. Lime water.

Experiment I.—*To contrast the effect of mixing sugar and powdered marble with that of mixing mercury and iodine.*

A. An experiment in *Lesson II. (I., A)* has shown that sugar may be dissolved in water and obtained again unchanged by removing the water by evaporation. Part B of *Experiment I., Lesson II.*, proved that marble does not dissolve in water, but that it does dissolve in diluted hydrochloric acid, and that the marble and the acid interact so as to produce at least two new substances, one of which is a colourless gas that produces a white solid in lime water, and the other is a deliquescent solid.

The object of the present experiment is to find an answer to this question: Is any new substance produced when sugar and powdered marble are rubbed together? The results of *Experiment I., Lesson II.*, are to be used in answering the question.

Mix, by rubbing together in a mortar, about equal quantities of powdered marble and powdered sugar—say about 10 grams (from one-third to one-half a test-tubeful) of each; place the mixture in a beaker, add about a couple of test-tubeful of water, warm for some minutes, shaking from time to time; let the solid

matter settle, and then pour the liquid through a filter paper placed in a funnel which is supported in a filter stand (see figure 2, p. 6), collecting in a basin the liquid that runs through the filter (this liquid is called *the filtrate*). Pour about two test-tubesful of water on to the solid left in the beaker, warm and shake thoroughly, allow to settle, and pour the liquid through the filter that was used before, collecting the filtrate in the same basin as before. Repeat this treatment with water until the liquid that runs through the filter ceases to taste sweet. Mix the filtrate; pour away about three-fourths of it; evaporate the remainder in a basin over a very small flame until the liquid becomes thick, *stirring constantly*; then remove the flame, and stir till solid matter forms (see below). Now remove the solid which remains in the beaker on to a piece of calico, and press it till it is dry; put the dried solid into a test-tube fitted with a cork and a bent tube as described in *Experiment I., B, Lesson II.* (see p. 8, fig. 4); pour a little diluted hydrochloric acid on to the solid; notice that effervescence occurs; let the gas that comes off bubble through some clear lime water in a test-tube, and notice that a white solid forms in the lime water. The results of this part of the experiment prove that the solid left after repeatedly treating the mixture of marble and sugar with hot water is unchanged marble.

When the filtrate obtained by treating the original mixture with hot water and pouring the liquid through a filter has evaporated to dryness (see above) (you must stir vigorously with a glass rod as the liquid becomes thick), notice that the dry substance has the appearance and the taste of sugar; put some of it into a test-tube fitted with a cork and a bent tube dipping into lime water, and pour a little diluted hydrochloric acid into the tube; you do not notice any effervescence, nor is a gas given off which produces a white solid in the lime water.

This experiment proves that each of the constituents of a mixture of sugar and powdered marble behaves towards water in the same way as it does when it is unmixed with the other constituent; and the experiment makes it very probable that no new substance is produced when powdered marble and sugar are mixed.

B. Is any new substance formed when mercury and iodine are mixed ?

If a new substance is formed by mixing mercury and iodine, the properties of the new substance will be different from the properties of its constituents; hence an examination of some property, or some properties, of mercury and iodine, followed by an examination of the properties of the product of mixing these substances, will enable you to answer the question proposed. Look carefully at mercury and iodine, and note the appearance of each. Place a little iodine, and a very little mercury, in separate test-tubes, add some water, and shake; the mercury is not affected visibly, but the water over the iodine acquires a faint yellow colour after shaking for a minute or two. Now add a little alcohol to very small quantities of mercury and iodine in different test-tubes, warm slightly, and shake for a few moments; the mercury is not altered, but the alcohol gradually acquires a yellowish red colour, which indicates that some of the iodine has dissolved in it.

The results so far obtained show that mercury and iodine can be distinguished one from the other by their appearances, and by their behaviours with water and with alcohol. If no new substance is formed when mercury and iodine are mixed, it will probably be possible to see particles of mercury and particles of iodine in the mixture, and if the mixture is shaken for a little time with water, we should expect the water to become slightly yellow, and we should also expect warm alcohol to acquire a yellowish red colour when shaken for some time with the mixture; moreover, if the iodine and the mercury retain their properties in the mixture, it should be possible to remove the iodine and to leave the mercury by warming and shaking with alcohol, pouring off the coloured liquid, and repeating this treatment several times. On the other hand, if the product of mixing mercury and iodine is a substance different from either of its constituents, that substance will not behave towards water, and alcohol, as a mere mixture of mercury and iodine would behave, and the appearance of the new substance will be more or less distinctly unlike that of either constituent.

Now place three or four flakes (not more) of pure, resublimed,

iodine in a dry, clean, mortar; add not more than two drops of alcohol (to cause solution of part of the iodine and so to bring it into closer contact with the mercury), and then about two drops of mercury. Rub the substances in the mortar with a pestle until a brownish green (or it may be a reddish grey) powder is formed¹; detach this powder, by means of a spatula, from any particles of mercury that are visible, place it in a test-tube, add some alcohol, warm, shake for a short time, and allow the solid matter to settle: if the alcohol is at all coloured, pour it off, add a little more alcohol, warm, and shake again. The alcohol is not coloured; hence no iodine has dissolved. Pour off the alcohol, add some water to the solid matter in the tube, and shake vigorously for some time; the water is not coloured. Therefore, the mercury and the iodine have interacted in such a way that something is formed which has at least some properties different from those of either mercury or iodine.

This part of the experiment should be contrasted with part A of the same experiment; in one of these experiments no new substance was produced by mixing certain definite substances, while in the other experiment the bodies that were mixed reacted so as to produce a new substance.

The product of mixing powdered marble and sugar is a *mixture*; the product of mixing mercury and iodine belongs to the class of *not-mixtures*. Or it may be said that chemical change is not brought about by mixing marble and sugar, but that chemical change occurs when mercury and iodine are rubbed together vigorously in presence of a few drops of alcohol.

¹ When mercury and iodine are rubbed together for a few minutes there is sometimes a sudden production of heat, violet vapours (of iodine) are given off, and a greyish red powder remains.

LESSON IV

EXERCISES ON THE CLASSIFICATION OF SUBSTANCES INTO
MIXTURES AND NOT-MIXTURES

Exercise I.—The solid A is composed of the solids *a* and *b* ; is A a mixture of *a* and *b*, or have *a* and *b* combined chemically to form A ?

You must observe some properties of *a* and *b* separately, and you must then determine whether *a* and *b* do or do not retain these properties in A, which has been made either by mixing *a* and *b*, or by causing these bodies to combine chemically. The properties of *a* and *b* which we shall observe are: (1) their behaviours towards water, and (2) their behaviours towards hydrochloric acid.

A. Shake with water *small* quantities of *a* and *b*, separately ; and note the results.

Does *a* or *b* dissolve ? Is any gas given off ? Does the substance sink in the water, or float, or partly sink and partly float ? Is any change produced in the colour or appearance of either substance, or in the colour of the water ?

Now warm the water in which you have placed *a* and *b* ; and note the results. Then shake with water a *small quantity* of A ; and, having noted the results, warm the water and again note what you observe.

If the behaviour of A with water is equal to the behaviour of *a* added to that of *b*, then A is a mixture of *a* and *b*. But if the behaviour of A with water is different from the sum of the behaviours of *a* and *b*, then A is not a mixture of *a* and *b* ; as you know that A is composed of *a* and *b*, you must conclude, in this case, that A is a compound.

B. Shake *small* quantities of *a*, *b*, and A, separately, with

about one-fourth of a test-tubeful of *concentrated* hydrochloric acid ; note the results. Then warm the acid in each tube, and note the results. Use the same kind of reasoning as in **A** to determine whether **A** is a mixture, or a compound, of *a* and *b*.

The following questions suggest the kind of observations you should especially make in this part of the exercise. Does *a*, *b*, or **A**, dissolve in the cold hydrochloric acid ? Does any of the three substances dissolve in the hot acid ? Is the colour of the acid changed ? Is any coloured or odorous gas given off ? (Warm some concentrated hydrochloric acid alone and smell the gas that comes off.) Do the substances sink in the acid, or float, or partly sink and partly float ?

Exercise II.—The solid **C** is composed of the solids *x* and *y* ; is **C** a mixture, or a compound, of *x* and *y* ?

The method to be employed is the same as in *Exercise I*, but we shall slightly alter the way of applying the method.

A. Heat, in *dry* test-tubes, small quantities of *x*, *y*, and **C**, separately ; and note the results.

Is there any change in the appearances of the substances ? Does any of them melt, or sublime ? Is any odorous or coloured gas given off ?

B. Mix small quantities of *x* and *y*, by pounding in a mortar.

Compare the appearance of this mixture with the appearance of **C**. Note what happens when you heat a little of this mixture in a dry test-tube.

Any change of appearance ? Any evolution of gas ? Does sublimation occur ?

Shake a little of the mixture with water. Then shake a little of the mixture with diluted hydrochloric acid ; and then warm. Note carefully what you observe in each case. Try the action of water, and of diluted hydrochloric acid, on **C**, and also on *x* and *y*, separately ; and note the results.

Does the whole, or only part, of the mixture sink in water ? Does **C** sink, or float, or partly sink and partly float, in water ? Is any gas given off when the mixture is warmed with diluted hydrochloric acid ? Is any gas given off when **C** is warmed with diluted hydrochloric acid ; if there is a gas, is it the same as that given off by the mixture ? Is any gas given off when *x*, or when *y*, is warmed with hydrochloric acid ; if there is a gas, is it the same as that given off by the mixture, or the same as that given off by **C** ?

Note to the Student

In recording the results of your observations in this exercise, and in exercises of a similar kind, it is advisable to use a method which shall bring together the results of the action of the same agent on the different substances, so that these results may be compared and contrasted. To record the results in parallel columns is probably the simplest plan. An example is appended.

PROBLEM. The substance P is either a mixture or a compound of the substances *m* and *n*; which is it? Examine the action of (1) heat, (2) diluted sulphuric acid, on the three substances.

OBSERVATIONS. The three substances were white solids.

Action of heat

P	<i>m</i>	<i>n</i>
No visible change; no gas given off; no smell.	No visible change; no gas given off; no smell.	No visible change; no gas given off; no smell.

Conclusion. P may be either a mixture, or a compound, of *m* and *n*.

Action of diluted sulphuric acid

P	<i>m</i>	<i>n</i>
Effervescence; gas given off colourless and odourless; when effervescence stopped, more acid produced more effervescence, but finally no effervescence was caused by fresh acid, and white solid remained.	No visible action; nothing apparently dissolved.	Effervescence; colourless odourless gas given off; whole of <i>n</i> eventually dissolved with effervescence.

Conclusion. P is a mixture of *m* and *n*.

The results of your examination of the substances given in this lesson should be entered in your note-book in the following form:—

I.	A.	a.	b.
Shaken with water; water then warmed	—	—	—
Shaken with conc. hydrochloric acid; then warmed	—	—	—

CONCLUSION.

II.

	C.	x .	y .	Mixture of x and y .	
<i>Effects of heating</i>	—	—	—	—	
	C.	Mixture of x and y .		x .	y .
<i>Effects of shaking with water</i>	—	—		—	—
<i>Effects of shaking with diluted hy- drochloric acid</i>	—	—		—	—
<i>Effects of warming with diluted hy- drochloric acid</i>	—	—		—	—

CONCLUSION.

LESSON V

NOT-MIXTURES DIVIDED INTO COMPOUNDS AND ELEMENTS.
TWO KINDS OF CHEMICAL CHANGE; BUILDING UP AND
BREAKING UP

Apparatus and materials required.—Porcelain crucible, about $1\frac{1}{4}$ inch deep, and lid. Small earthenware crucible about $1\frac{1}{4}$ inch deep. Small shallow earthenware tray, about 4 inches diameter. Magnesium ribbon. Emery paper. Two pill-boxes with lids, small shot, and tinfoil. Piece of stout iron wire about 3 inches long. Small pieces of lead. Triangle. Two dry test-tubes of hard glass; two corks to fit these. Rat-tail and cutting files. Two pieces of glass tubing about $\frac{1}{8}$ inch internal diameter and 6 to 8 inches long. Trough for collecting gas over water. Splints of wood. Dry red lead. Red oxide of mercury.

It will save time if Experiment II. is started before Experiment I., and Experiment I. is performed while the lead is being heated in Experiment II.

Experiment I.—To find out something about the change which occurs when magnesium is burnt in air.

Burn a little bit of magnesium ribbon, by holding one end in the Bunsen flame for a moment; notice the white powder that is produced. Chemical change has evidently taken place.

Has this white solid been drawn out of the magnesium—as sugar was withdrawn from a mixture of marble and sugar in Experiment I., Lesson III.; by the action of water—or has the solid been formed by the chemical combination of the magnesium with something else? Has the magnesium been broken up into this white substance and something else you do not see; or has

the magnesium combined with some other substance and so formed the white powder?

To answer this question approximately it will be necessary to determine whether the white solid obtained by burning magnesium weighs the same as, more than, or less than, the magnesium.

Counterpoise a clean, dry, porcelain crucible with a lid.

The crucible should be about 30 mm. (about 1½ inch) deep by about the same diameter at the top. The counterpoising may be done by placing a pill-box on the other pan of the balance, and putting small shot and little pieces of thin tinfoil into this box.

Clean a piece of magnesium ribbon about 150 to 200 mm. (about 6 to 8 inches) long, by rubbing it with emery paper; arrange the magnesium in the crucible as shown in figure 8, but wrap the folds of the ribbon more closely together than is shown in the figure; counterpoise the crucible with the magnesium in it and the lid on. Now remove the lid of the crucible and hold it in the crucible tongs; set the crucible on a pipeclay triangle resting on a tripod; and heat the crucible to full redness by a Bunsen lamp. As soon as burning of the magnesium

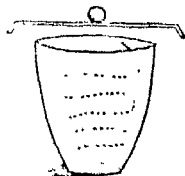


FIG. 8

begins bring the lid so close to the crucible that the white smoke produced is caught on the lid, at the same time leaving a little space for the entry of air into the crucible (see the figure). If the burning nearly ceases remove the lid, *for a moment*, further from the crucible; if the burning proceeds so rapidly that smoke escapes freely bring the lid nearer the crucible. When the whole of the magnesium is burnt place the lid *upside down* on the crucible (this is to prevent the falling off from the inside of the lid of the white solid that has collected on it); allow the crucible and its contents to cool; then place it on the pan of the balance, and place on the other pan the counterpoise whose weight was equal to that of the crucible, lid, and magnesium taken together.

The crucible, lid, and burnt magnesium together weigh more than the crucible, lid, and unburnt magnesium weighed.

It seems, then, that while the magnesium burnt it laid hold of some other substance, or substances.

Did the burning magnesium take something away from the vessel wherein it was burnt?

Thoroughly clean the crucible and lid with a dry cloth; place them on the pan of the balance, and on the other pan place the counterpoise whose weight is known to be equal to that of the crucible and the lid at the beginning of the experiment. The weight of the crucible and lid is the same as before the magnesium was burnt; therefore nothing has been removed by the burning magnesium from the vessel wherein it was burnt.

This experiment makes it very probable that when magnesium is burnt in air the magnesium combines with the air, or with some constituent of the air, to form a white powder. The burning of magnesium is probably a process of building up.

Experiment II.—*To find out something about the change that occurs when lead is heated in air.*

When lead is strongly heated in the air for some time it is changed into a yellowish red powder; is this a case of building up or breaking up?

Place six or eight small *thin* pieces of lead, each about the size shown in the margin, in a clean dry earthenware crucible about $1\frac{1}{4}$ inch deep, lay a bit of stout iron wire about 75 mm. (3 inches) long across the crucible, and counterpoise the crucible with the lead and the iron wire on it. Put the crucible on a pipeclay triangle resting on a tripod, and bring a Bunsen burner under the tripod with the flame arranged so that the bottom of the crucible becomes visibly hot after a minute or two. Continue to heat in this way for about twenty-five or thirty minutes, stirring the lead *cautiously* from time to time with the piece of iron wire, and taking care that nothing is spilt from the crucible or lost by dropping from the stirrer. (The reason for stirring is to expose fresh surfaces of the hot lead to the action of the air.)

When a fair quantity of a yellowish red powder has formed on the surface of the lead (which will be after the heating has been continued for nearly thirty minutes) remove the source of heat, place the stirrer in the crucible, and let the whole cool. When

quite cold, counterpoise the crucible and its contents, including the stirrer; there is a slight increase in weight.

The result of this experiment makes it probable that when lead is heated in the air it combines with the air, or with some constituent of the air, to form a yellowish red powder; the formation of this powder, which may be called burnt lead, is probably a process of building up.

Experiment III.—To make a further examination of what occurs when lead is heated in air.

The object of this experiment is to find out more about the process that occurs when lead is heated in the air, which process is probably one of building up.

If the change brought about by heating lead in air consists in a combination of the lead with the air, or with part of the air, it may be possible to get the air out of the burnt lead.

When lead is roasted in a stream of air at a low red heat red lead is gradually formed; if the temperature is raised litharge is produced.

Arrange a dry test-tube, made of hard glass, with a good cork and exit-tube as shown in figure 9. Fill this tube to about one-eighth with dry red lead; remove the cork and counterpoise the

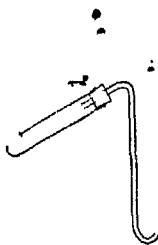


FIG. 9

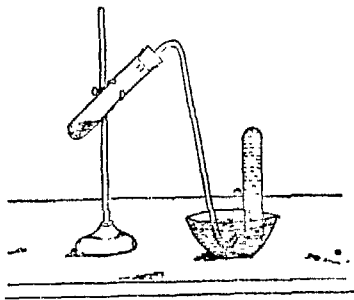


FIG. 10

tube and red lead. Again put in the cork, support the tube, by means of a clamp, in the position shown in figure 10, allowing the lower end of the tube to dip under water in a fair-sized basin, or in a shallow earthenware tray. Have ready a few thin slips of wood. Now heat the tube by a small flame; beginning

from the upper surface of the red lead and slowly heating downwards, and taking care that the heat is applied very gradually (to prevent the tubing cracking), and that the lamp is not brought near enough the cork to char it. The air in the tube will expand and will be driven out; you will see it bubbling up through the water in the basin. After a few minutes the bubbles of air will come off very slowly; now raise the Bunsen flame; air will likely come off more freely for a few moments, but will soon slacken again. When this second slackening of the air-bubbles is noticed, bring another Bunsen lamp beneath the lower end of the tube. After a short time (say five minutes or so) you will probably notice that bubbles of some kind of air or gas are coming off; fill a test-tube with water, close the mouth with the thumb, invert the tube, bring the mouth under the water in the basin, remove the thumb, and move the mouth of the test-tube over the end of the delivery-tube from which the bubbles are escaping. Hold the test-tube in this position until it is filled with the air, or gas, that is coming from the very hot red lead; then slip the thumb under the water, and place the thumb over the mouth of the test-tube; remove the test-tube (closed by the thumb) from the water; set fire to one of the thin slips of wood, and when it has burnt for a moment gently blow out the flame so that the wood smoulders but does not burn brightly; remove the thumb from the mouth of the test-tube and at once plunge the glowing piece of wood into the tube:—the wood burns brightly in the gas, or air, in the test-tube. Continue to heat the red lead for some time longer—say, for ten minutes—so as to make sure that a fair quantity of this combustion-supporting gas is removed from it; then lift the end of the delivery-tube out of the water, remove the Bunsen lamps, and let the test-tube and its contents cool completely. When the tube is quite cold remove the cork, and counterpoise the tube and its contents; you notice that the weight is slightly less than it was before heating. You will also notice that some of the red lead has been changed into a yellow solid (this is litharge).

This experiment shows that when red lead is strongly heated it loses weight, and that a colourless gas is given off which is not ordinary air, inasmuch as this-gas causes a smouldering slip of wood to burn brightly.

Now red lead is produced by heating lead in a stream of air ; and we know, from *Experiment II.*, that this process is accompanied by an increase of weight.

The results of *Experiments II.* and *III.* make it very probable that the formation of red lead by heating lead in air is a process of building up, and that this process consists in the combination with the heated lead of a constituent of the air which differs from ordinary air in that it supports combustion more vigorously than ordinary air does.

What experiments do you think should be required in order to prove this conclusion satisfactorily?

Experiment IV.—*To examine the effect of heat on burnt mercury.*

You are given a red powder, which you are told is produced by heating mercury to its boiling-point in air for a long time.

Repeat *Experiment III.*, using this red powder (burnt mercury) in place of red lead, and heating in a tube of *hard glass*. Apply the test of a smouldering chip of wood to the gas that comes off ; so far as this test can tell you, the gas is the same as that you obtained from red lead. Notice the mercury that sublimes in the tube wherein you have heated the burnt mercury. Prove that the tube and its contents weigh less after heating than the tube with the burnt mercury in it weighed before heating.

In this experiment we have another process of breaking up ; the burnt mercury is broken up by heat into mercury, and a colourless gas called oxygen.

Experiments I. and *II.* of this lesson are illustrations of processes of building up ; *Experiments III.* and *IV.* are illustrations of processes of breaking up.

Compounds are those not-mixtures which have been broken up into two or more unlike constituents ; compounds are generally capable of combining with other not-mixtures to form more complex compounds.

Elements are those not-mixtures which have not been broken up into unlike parts or constituents ; elements combine with other not-mixtures to form compounds.

LESSON VI

EXERCISES ON THE TWO KINDS OF CHEMICAL CHANGE WHICH THOSE SUBSTANCES THAT ARE NOT-MIXTURES MAY UNDERGO

Apparatus required.—Two thin earthenware crucibles, about $2\frac{1}{2}$ inches deep. Two stirrers of stout iron wire. Two pill-boxes with lids; small shot; tinfoil.

The solids A and B, which are not-mixtures, both undergo chemical change when they are heated in the air; find out, as conclusively as you can, whether the change which each undergoes is a process of breaking up or building up.

The experiments which can be made at this stage will not suffice for a perfectly conclusive solution of this problem.

Begin by heating a little of each substance in a small thin earthenware crucible, about 60 mm. ($2\frac{1}{8}$ inches) deep. Note what you see; bring a lighted taper, and then a smouldering slip of wood, near the surface of each substance after the crucible is red hot (see *Experiment I., Lesson II.*, where a lighted taper was used as a test for the gas produced by pouring hydrochloric acid on to marble; and *Experiment III., Lesson V.*, where a smouldering chip of wood was used as a test for oxygen).

Then place a little of A (about 5 grams) in a thin earthenware crucible, about $2\frac{1}{2}$ inches deep, with a stirrer made of a piece of stout iron wire; counterpoise; heat for 10 or 15 minutes, stirring now and again, taking great care that nothing is lost by the process; note what visible change occurs; let cool, and counterpoise again.

Then perform a similar experiment with about 5 grams of B.

Write out an account of your results, and indicate the conclusions you draw from these results.

LESSON VII

RUSTING OF IRON. BURNING OF PHOSPHORUS. METHODS OF
INVESTIGATING CHEMICAL CHANGES

Apparatus and materials required.—Clean iron filings.¹ Phosphorus. Lime water. Precipitated oxide of mercury dried at 100°. Piece of stout copper wire about 18 inches long. Muslin. Earthenware trough. Glass jar about 6 inches high by 1½ inch diameter. Measuring vessel graduated in 10th c.c. Two dry test-tubes, with caoutchouc cork to fit; dry test-tube of hard glass, fitted with good cork and exit-tube, to collect gas over water. Tapers. Splints of wood. File.

Experiment I.—*Iron rusts when it is kept in moist air; what chemical change occurs? Is the rust composed of iron and something else; or is the iron separated, in the process of rusting, into unlike constituents, of which rust is one?*

To find answers to these questions you must allow iron filings to rust in a portion of air cut off from the general atmosphere, and under conditions such as shall enable you to determine whether any air disappears during the rusting process, and if any air disappears, what proportion the volume of air that disappears bears to the total volume of the air wherein the rusting has taken place; you must also be able to examine the properties of the air that remains when the experiment is finished.

From a piece of fairly stout copper wire make a little stand of the shape shown in figure 11; the stand should be about 125 mm. (about 5 inches) high; the twisted

FIG. 11

¹ Iron filings may be cleaned by immersing them for a short time in diluted sulphuric or hydrochloric acid, then washing repeatedly and quickly in running water, and drying by pressing in calico.

part, which serves as a support, should be not more than 30 mm. (say $1\frac{1}{4}$ inch) across. Put about a test-tubeful of clean iron filings into a little muslin bag, and wet the filings *thoroughly*, by keeping the bag beneath water for *about five minutes*, and pressing it several times with the fingers; support the bag on the hook of the little stand, place the stand in a flat earthenware trough, and cover it with a small glass jar about 150 mm. high and about 45 mm. diameter (about 6 inches by $1\frac{3}{4}$ inch); pour water into the trough to the depth of about 25 mm. (1 inch), and, by inclining the jar to one side, allow the water to enter the jar so that the level of the water inside the jar is the same as the level outside (see figure 12). Make a slight

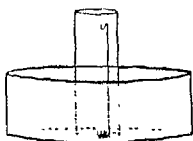


FIG. 12

scratch with a file on the outside of the jar at the level of the water; and set the whole apparatus aside until next day. (See Lesson VIII.)

Experiment II.—*What change occurs when phosphorus burns in air? Is the burnt phosphorus composed of phosphorus and something else? Does the phosphorus withdraw anything from the air in which it burns?*

In *Experiment I., Lesson V.*, you found that while magnesium burnt in air it probably laid hold of and combined with the air, or something in the air. The process that occurs when phosphorus burns in air may be like the burning of magnesium; if the processes are similar, then burning phosphorus probably combines with a portion of the air that surrounds it, or with some constituent of the surrounding air. You must endeavour to find out whether or not a change of that kind takes place.

Cut three small pieces of phosphorus, each about 3 mm. ($\frac{1}{8}$ th inch) square; dry the phosphorus by pressing the pieces *very gently* between filter paper, and at once put them into a dry test-tube, and close the tube firmly by a good caoutchouc cork.

You must be very careful in handling phosphorus, as it is an extremely inflammable substance, and burns caused by phosphorus are hard to heal. Always keep phosphorus under water, and cut it under water.

Make a *very slight* mark, with a file, on the outside of the tube opposite the inner end of the cork. Hold the tube, in a test-tube holder, in a slightly slanting position, and heat the part of the tube where the phosphorus is *very gently over a low flame until the phosphorus just begins to burn* (see figure 13); then remove the flame, and at once turn the tube so that the corked end points nearly downwards. When the phosphorus ceases to burn bring the tube back to its original position; heat the part where the phosphorus is *gently* for a few moments, and shake the phosphorus about in the tube (turning the closed end of the tube downwards). Repeat this process of heating the phosphorus *slightly*, and turning the tube about so that all the air in it may be brought into contact with the glowing phosphorus. *But take care that the phosphorus is heated only slightly, and never for more than a few moments at a time; as, if you heat too much or too long the cork may be blown out of the tube, and the burning phosphorus may get on to your hands. Also take care that the glowing phosphorus does not come into contact with the cork.*

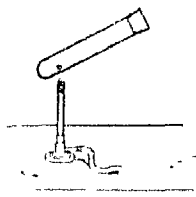


FIG. 13

Now let the tube get quite cold; then plunge the corked end under *distilled* water in a basin, and gently withdraw the cork, taking care that the mouth of the tube is under the water all the time. Water rushes into the tube. Shake the tube slightly (see that the mouth is kept under the water while you do this); then depress the tube until the level of the water outside is the same as the level inside, and close the mouth of the tube firmly, under the water, with the thumb. Reverse the tube, keeping the thumb pressed firmly on to the mouth, and mark the level of the water in the tube by making a slight scratch on the tube with a file. Light a *small* taper, or a *thin* chip of wood; remove the thumb, and plunge the lighted taper into the tube; the taper goes out. At once withdraw the taper and pour some clear lime water into the tube; the lime water remains clear.

Now determine, with the help of a narrow vessel graduated in $\frac{1}{10}$ ths of a c.c., (i.) the volume of the water required to fill the tube to the mark which indicates the position occupied by the

inner end of the cork when the phosphorus was burnt in the tube, and (ii.) the volume of the water which rushed into the tube when the cork was withdrawn: (i.) expresses the volume of the air that was in the tube when the burning began, and (ii.) expresses the volume of the air, or the constituent of the air, that was removed by the phosphorus while it burnt.

If your experiment is done carefully it shows that about one-fifth of the volume of the air originally in the tube was removed by the burning phosphorus. The experiment also shows that the air left in the tube when the burning was finished, which air amounted to about four-fifths of the original volume of air, was not common air, neither was it oxygen (compare Experiment III., Lesson V.), neither was it the air or gas produced by the reaction of hydrochloric acid and marble (compare Experiment I., B, Lesson II.).

Your experiments on heating lead in air (*Experiment II., Lesson V.*), and strongly heating red lead (*Experiment III., Lesson V.*), which is itself the product of roasting lead in a current of air, made it very probable that the change of lead to red lead consists in the withdrawal of oxygen from the air by the hot lead. If the change that takes place when phosphorus is burnt in air is similar to the change which occurs when lead is burnt in air, then the burning phosphorus probably withdraws oxygen from the air; if this is what occurs, you might expect that common air would be re-formed by adding to the gas that remains when phosphorus has burnt in an enclosed quantity of air, a volume of oxygen equal to the volume of the air, or gas, that has disappeared during the burning. Let us try whether this guess is correct or not.

Experiment III.—Repeat *Experiment II.*, using another dry test-tube; but when you have removed the cork from the tube standing mouth downwards under water in a basin (you need not put distilled water in the basin in this experiment, nor need you mark the space occupied by the cork inside the tube), then, instead of placing the thumb over the mouth of the tube and reversing it, hold the tube with its mouth under water in the

left hand, while you fill another similar test-tube with the water in the basin and you reverse this tube in the water. Now bring the two tubes close alongside one another; then slowly depress the closed end of the tube that contains gas while you keep the mouths of the tubes in such a position that the gas passes from the tube in which the phosphorus was burnt and ascends, bubble by bubble, into the other tube (see figure 14). Transfer the whole of the gas, in this way, to the second tube, taking care that none escapes; then support the tube with the gas in it, by a wooden clamp, with its mouth still under the water in the basin.

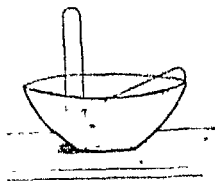


FIG. 14

The transference of the gas is effected for the purpose of separating it from the small pieces of phosphorus that remain when the burning is finished; if any phosphorus is left in the tube, burning may begin again when oxygen is passed into the tube in the next part of the experiment.

Now arrange a dry test-tube of *hard glass* containing a little burnt mercury (oxide of mercury)¹ with a cork and delivery-tube, as shown in figure 15, supporting the tube in a clamp; heat the lower end of the tube, at first gently, and after a few minutes more strongly. When the heating has been continued for some minutes bring a smouldering chip of wood close to the open end of the delivery-tube; if the wood at once bursts into flame you may take it that all the air is driven out of the apparatus and that oxygen is being given off; but if the wood does not at once burn brightly, continue to heat the tube until another piece of smouldering wood bursts into flame as soon as it is brought close to the open end of the

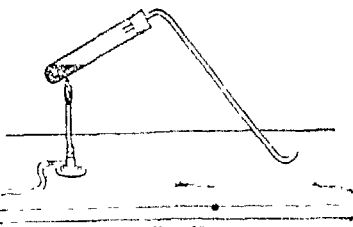


FIG. 15

¹ Yellow oxide of mercury, prepared by precipitation and dried at 100°, should be used, as oxygen is given off at a lower temperature from this than from the red, crystalline oxide.

exit-tube. When oxygen is coming off freely bring the end of the tube from which oxygen is issuing under the test-tube that contains the gas which was left when the phosphorus was burnt in air, which tube is standing mouth downwards in water, *continuing to heat the tube that contains the oxide of mercury as you are doing this*. Let the oxygen bubble into the test-tube until the tube is filled with the gas; then remove the apparatus that is supplying oxygen, slip the same caoutchouc cork which you used in the first part of the experiment into the tube standing mouth downwards in the water, and shake the tube several times. Get ready a smouldering chip of wood, and have a very small taper, or a very thin slip of wood, by your side ready to be lighted. Remove the caoutchouc cork, and at once plunge the smouldering wood into the tube; the wood behaves as it does in ordinary air. Quickly withdraw the wood, and at once bring the very small lighted taper, or the thin slip of wood burning freely, a little way into the tube; the taper burns as it did before you put it into the tube.

The results of this experiment tend to confirm the guess made at the end of last experiment; namely, that ordinary air would be produced by adding to the gas that remained when phosphorus had burnt in an enclosed volume of air enough oxygen to bring back the total volume to that of the air which surrounded the phosphorus before burning began.

The results of Experiments II. and III. indicate that ordinary air is formed by mixing one volume of oxygen with four volumes of the gas, or air, that remains when phosphorus is burnt in an enclosed quantity of air.

Assuming this conclusion to be accurate—it is not completely proved by your experiments—common air seems to consist of two gases, present in the proportion of (about) one volume of a gas wherein a burning taper, or a glowing slip of wood, burns very brilliantly, and (about) four volumes of a gas which stops the burning of a lighted taper, and which does not produce any solid matter when shaken with lime water.

The gas which forms about one-fifth of common air, by volume, is, as you know, called *oxygen*; the other gas, which forms about four-fifths of air, by volume, is called *nitrogen*.

Recalling the facts that (i.) a burning taper burns very brightly in oxygen (*Experiments III. and IV., Lesson V.*), (ii.) a burning taper is extinguished in nitrogen, and (iii.) a burning taper burns in the gas prepared by mixing four volumes of nitrogen with one volume of oxygen neither more nor less brightly than it burns in air, you may conclude, provisionally, that oxygen and nitrogen retain their distinctive properties in air, and that air is probably a mixture, not a compound, of these gases.

LESSON VIII

RUSTING OF IRON—*continued*. PREPARATION OF OXYGEN, AND EXAMINATION OF SOME OF THE PROPERTIES OF THIS GAS

Apparatus and materials required.—Two pieces of stout copper wire, each about 12 inches long; some thin copper wire. Clean iron filings. Muslin. Earthenware trough. Small earthenware tray. Glass tube about 7 inches long by 1 inch diameter. Measuring vessel divided into 10 c.c. Measuring tape. Four thin glass jars about 6 inches high by 3 inches diameter. Hard glass tube, with cork and exit-tube, to collect gas over water. Thin cardboard. Two deflagrating spoons. Tapers. Dry chlorate of potassium and black oxide of manganese. Sulphur. Charcoal. Magnesium ribbon. Sodium. Red and blue litmus solution:

Experiment I.—*Continuation of the experiment on the rusting of iron begun in last lesson.*

Turn back to the experiment on the rusting of iron which you began in the last lesson.

The water has risen in the jar containing the rusting iron and air. Pour water into the earthenware dish until the level of the water outside is the same as the level inside the jar, and make a slight scratch with a file on the outside of the jar at the level of the water. Measure the distance from the scratch to the closed end of the jar; and then measure the distance from the scratch to the mark you made on the jar in the last lesson to indicate the level of the water at the beginning of the experiment. You find that about one-fifth of the volume of air originally in the jar has disappeared.

Experiment II. of Lesson VII. indicated that phosphorus burning in an enclosed volume of air removes a constituent of the air which is present to the amount of about one-fifth of the

whole volume of air wherein the phosphorus is burnt, and that the four-fifths which remain of the original volume of air consist of another gas that extinguishes a burning taper.

The results of the present experiment, so far as that experiment has gone, show a distinct resemblance to the results obtained by burning phosphorus in air. We must examine this resemblance more fully. And first of all we must find out whether moist iron is able to withdraw anything from the gas that remains in the jar wherein the rusting process has gone on, or whether that gas is without action on moist iron.

It will be necessary to decant the gas, or air, from the jar into another vessel in which you have placed a fresh quantity of moist iron.

Make a small stand of fairly stout copper wire, like that in the jar, but of such a size that it will go easily into a test-tube about 175 mm. long and 25 mm. diameter (7×1 inch); the height of the stand should be rather less than the length of the test-tube. Put about half a test-tubeful of *clean* iron filings into a muslin bag, and soak the bag *thoroughly* in water for about five minutes, squeezing the bag with the fingers several times under water to get all the air bubbles out of the material. Hang the bag on the hook of the stand, cover the stand with a test-tube about 175 mm. long by 25 mm. diameter (7×1 inch), invert the tube with the stand in it, and fill the tube with water. Now cover the mouth of the tube with a slip of *thin* cardboard, taking care that no bubbles of air remain in the tube; press the cardboard firmly on to the mouth of the tube by the thumb, invert the tube, bring it mouth downwards under the water in the earthenware trough wherein the jar with the rusted iron in it is standing, remove the cardboard, and secure the tube by a wooden clamp. Now pour water into the earthenware trough until it is nearly full. *Very cautiously* raise the test-tube with the iron in it until the mouth of the tube is only a little way under the water, but *be certain that no air gets into the tube*; and move the tube, held in the clamp, near to one side of the earthenware trough. Now move the jar wherein the process of rusting has gone on (always keeping it mouth downwards under water) to such a distance from the inverted test-tube that when you depress

the closed end of the jar the gas in the jar will escape and bubble up into the inverted test-tube. *This part of the operation must be done very carefully and slowly (see figure 16).*

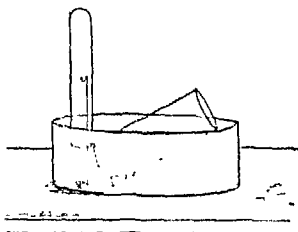


FIG. 16

Allow the gas to pass from the jar into the test-tube until the level of the water inside the tube is the same as the level outside, when the mouth of the tube is kept a very little way under the water in the trough; then turn the jar mouth downwards under water, and move it to one side of the trough.

Slip a small earthenware tray under the mouth of the tube with the moist iron in it; place one hand on the top of the tube, and with the other hand remove the tray, with the tube standing mouth downwards under water in the tray, and set aside until the next day (see *Lesson IX.*)

If there is any gas left in the jar it will be advisable to examine it by the lighted taper test; for this purpose slip a piece of thin cardboard under the mouth of the jar, press the cardboard firmly against the jar with the fingers, remove the jar from the water, invert it, light a taper, remove the cardboard, and at once plunge the lighted taper into the gas in the jar: the taper goes out.

The gas left in the vessel wherein iron has rusted extinguishes a lighted taper, and in this respect it behaves in the same way as the gas which remained when phosphorus had burnt in air. (See forward, Experiment I., Lesson IX.)

Now make more accurate measurements than those made at the beginning of this experiment of the volume of air in the jar when the rusting process began, and the volume of air, or gas, that was left in the jar when the process was stopped; using a narrow vessel graduated to $\frac{1}{16}$ ths of a c.c. for measuring the water. (The marks you cut on the jar will enable you to make the measurements that are necessary.) The result is that approximately one-fifth of the original volume of air has been removed by the rusting iron.

Experiment II.—*Preparation of oxygen and examination of some properties of this gas.*

Preceding experiments have shown that air contains at least two different gases, in one of which—*oxygen*—a burning taper burns very brightly and a smouldering chip of wood bursts into flame, while the other—*nitrogen*—extinguishes a burning taper plugged into it. Your experiments have also made it very probable that when lead is heated in air the lead slowly combines with oxygen in the air (*Experiments II. and III., Lesson V.*), that when phosphorus is burnt in air the phosphorus combines with oxygen in the air (*Experiment II., Lesson VII.*), and that the rusting of moist iron in air consists in the combination of the iron with oxygen in the air (*Experiment I., Lesson VIII.*).

It is advisable to prepare this gas, oxygen, which plays so important a part in processes of combustion, and to become acquainted with some of its properties.

The substances from which small quantities of oxygen were prepared in Lesson V. were themselves produced by heating metals, namely lead and mercury, in air. There are several other substances formed by roasting metals in air from which oxygen can be obtained by the action of heat; but oxygen is most easily prepared by heating a compound called *potassium chlorate*, mixed with some *black oxide of manganese*.

Make a mixture of about three parts dry powdered potassium chlorate with one part dry powdered manganese oxide.¹ Fit a test-tube of *hard glass* with a good cork carrying an exit-tube as shown in figure 17, and fill the tube to about one-third with the mixture of potassium chlorate and manganese

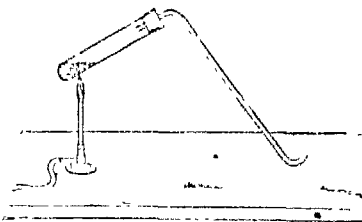


FIG. 17

¹ A very small quantity of this mixture should be heated in a test-tube to determine whether oxygen comes off quietly; manganese oxide is sometimes adulterated with carbonaceous matter, and such adulterated material is extremely dangerous if used in making oxygen.

oxide. Arrange the test-tube in a clamp¹ with the end of the exit-tube dipping under water in an earthenware dish, as shown in figure 18. Completely fill with water four jars made of thin

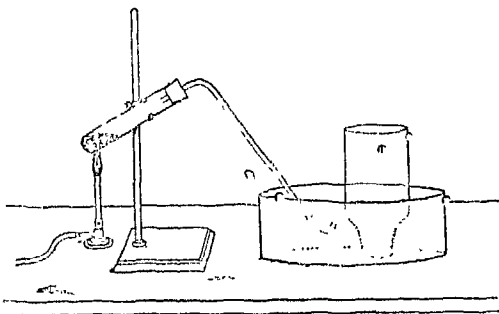


FIG. 18

glass, each about 150 mm. high and 75 mm. diameter (about 6 x 8 inches); cover the mouths of the jars with pieces of cardboard, invert the jars in the water in the earthenware dish, taking care that air does not enter the jars, and remove the cardboards.

Now heat the tube containing the mixture of potassium chlorate and manganese oxide, beginning with the upper part of the tube (taking care not to char the cork), and waving the flame under and around the tube; if the tube is heated rapidly at one part it will probably crack. When the tube has been gradually raised towards red heat, by moving the flame about and now and again allowing it to play on one part of the tube for a moment, lower the flame somewhat and let it heat the upper layers of the mixture. Bubbles of gas will soon be seen rising through the water in the dish; when gas is coming off pretty freely move one of the jars over the end of the delivery tube, and hold it there till it is filled with the gas; then remove the jar, reverse it, and cover its mouth with a piece of cardboard, on which you had better place some fairly heavy substance to prevent the cardboard being blown away. Fill the other three jars, in

¹ If a clamp is not at hand the tube may be laid across a tripod one foot of which is placed on a block of wood, so that one side of the tripod is tilted upwards.

succession, in the same way; then remove the delivery tube from the water, and lastly take away the Bunsen lamp from beneath the tube containing the mixture: if the lamp is removed while the end of the delivery tube is under the water, the water will probably run back into the tube and crack it.

Note.—In filling the jars with oxygen care must be taken to move the Bunsen burner gradually towards the lower end of the tube, so that fresh portions of the mixture of potassium chlorate and manganese oxide may be acted on by the heat.

Place a little powdered sulphur in a deflagrating spoon, set fire to the sulphur by holding the bowl of the spoon in the flame of a Bunsen lamp, and plunge the burning sulphur into one of the jars of oxygen. Describe what you see. When the burning is finished pour some *distilled* water into the jar, shake vigorously, cover the jar with a glass plate or a piece of cardboard, label it 'sulphur,' and set it aside.

Fasten three or four thin slips of charcoal to a stout copper wire, using thinner copper wire for fastening the charcoal; set fire to the charcoal in a Bunsen flame, and at once bring it into the second bottle of oxygen. Describe what you see. When the burning is finished pour some *distilled* water into the jar, and set it aside, after shaking thoroughly, covering the jar, and labelling it 'carbon.'

Set fire to a piece of magnesium ribbon, held in crucible tongs, and bring the tip of the burning magnesium into a jar of oxygen; combustion proceeds rapidly, and brilliantly white light is given out. When the burning is finished pour some *distilled* water into the jar, shake well, cover, label 'magnesium,' and set aside.

Cut a little piece of sodium from the inside of a lump,¹ put it into a *clean* deflagrating spoon, heat the bowl of the spoon in a Bunsen flame until the sodium melts and begins to burn (a high temperature, and heating for some minutes, will be required), and at once plunge the spoon into the fourth jar of oxygen. Describe what you see. When combustion is completed shake

¹ In handling sodium take care that your fingers are quite dry; sodium reacts violently with water.

the spoon vigorously, so that any burnt sodium adhering to it may fall into the jar; then pour *distilled* water into the jar, shake up, cover, label 'sodium,' and set aside.

The substance burnt in each of these processes of combustion in oxygen was an element; the products of the burnings are compounds of the elements sulphur, carbon, magnesium, and sodium, with oxygen; these compounds are called *oxides* (oxide of carbon, oxide of sulphur, &c.).

The oxides of carbon and sulphur produced in the combustions are gases; the oxides of magnesium and sodium are solids. Oxide of magnesium dissolves only slightly in water; the other three oxides dissolve easily in water.

Now turn back to the four jars containing solutions in water of the oxides formed in the combustions; only a small quantity of the magnesium oxide will have dissolved in the water. Pour a little of the solution of the oxide of sulphur into a *clean* test-tube, and add a few drops of red litmus solution; to another small quantity of the solution of the same oxide add a little blue litmus solution. Note the visible results. Make two similar experiments with each of the other three solutions of oxides, and note the results.

Arrange your results in the following form:

	Solution in water of Oxide of			
	<i>Sulphur</i>	<i>Carbon</i>	<i>Magnesium</i>	<i>Sodium</i>
Effect on red litmus	—	—	—	—
" " blue "	—	—	—	—

The four oxides fall into two classes, as regards the visible action of aqueous solutions of them on litmus solution. We shall learn more about these two classes of oxides in *Lesson XI.*, and in subsequent lessons.

LESSON IX

RUSTING OF IRON—*concluded*. PREPARATION AND SOME PROPERTIES OF THE GAS PRODUCED BY DISSOLVING IRON, ZINC, OR MAGNESIUM IN DILUTED SULPHURIC OR HYDROCHLORIC ACID. METHODS OF INVESTIGATING CHEMICAL CHANGES.

Apparatus and materials required.—Flask, about 8 oz., with caoutchouc cork, funnel tube, and exit-tube to collect gas over water. Earthenware trough, and three small trays. Four thin glass jars; three about 6 by 3 inches, and one rather smaller. Clean iron filings. Granulated zinc. Magnesium ribbon. Tapers. Lime water. Sulphuric acid diluted with ten times its volume of water. Hydrochloric acid diluted with three times its volume of water.

Experiment I.—*Conclusion of the experiment on the rusting of iron begun in Lesson VII. and continued in Lesson VIII.*

Turn back to the experiment on the rusting of iron which you carried to its second stage in the last lesson (see p. 36).

An examination of the apparatus you set aside will show that there has been no change in the level of the water in the tube; that is to say, the process of the withdrawal from the air of a constituent of the air, by the rusting iron, was completed in the first stage of your experiment, and the gas which remained when the air-constituent in question was withdrawn has not entered into combination with the fresh quantity of moist iron.

Now withdraw the little stand, with the bag containing the iron filings, from the test-tube, without letting air into the tube; this can be done by moving the little tray, with the tube mouth downwards in it, into an earthenware trough which is filled with water, then holding the tube nearly horizontally under the water in the trough, and gradually drawing out the stand.

Cover the mouth of the tube, under the water, with a piece of thin cardboard, reverse the tube, and plunge a *small* lighted taper into it; the taper goes out. *At once* withdraw the taper, pour a little clear lime water into the tube, and shake; the lime water remains clear.

These results are in keeping with those obtained in *Experiment II.* of *Lesson VII.*, wherein it was shown that the gas which remains when burning phosphorus has withdrawn oxygen from the air extinguishes a burning taper and has no visible effect on lime water. Examine the iron in the little muslin bag: it has not rusted.

Now write out a full account of your experiments on the rusting of iron, and the burning of phosphorus, in air, and state clearly what conclusions you draw from the results obtained.

Experiment II.—*Preparation, and some properties, of the gas that is given off when zinc, magnesium, or iron dissolves in diluted sulphuric acid, or in diluted hydrochloric acid.*

A. Pour into each of three test-tubes enough diluted sulphuric acid (concentrated acid diluted with about ten times its bulk of water) to fill the tubes to about one-fourth. Into one tube drop some *clean* iron filings, into the second a few thin pieces of granulated zinc, and into the third several small pieces of magnesium ribbon. Effervescence takes place in each case (in which tube is the effervescence most rapid?); the gases given off are colourless. When gas has been coming off for a minute or so, bring a lighted taper to the mouth of each tube; and repeat this after the lapse of a short time. The gas escaping from the tubes takes fire, probably with a slight explosion; this gas is evidently very different from oxygen, nitrogen, or carbon dioxide (the gas produced by adding hydrochloric acid to marble).

B. Repeat experiment A, but use diluted hydrochloric acid (about three parts water to one part conc. acid) in place of diluted sulphuric acid. Gas is given off in each tube; and the gas behaves towards a lighted taper like the gas produced when sulphuric acid was employed.

C. Fill a test-tube with diluted sulphuric acid (one part conc.

acid to about ten parts water), invert the tube in a small basin containing diluted sulphuric acid, throw a few small thin pieces of zinc into the basin, move the test-tube so that its mouth is over the pieces of zinc, and hold it there until the tube is filled with the gas that is coming off; then quickly bring the tube, mouth downwards, to a Bunsen flame. The gas takes fire and burns with a scarcely perceptible flame.

Repeat the experiment just described, but use *clean* iron filings in place of zinc; the result is the same as before.

• Fill a test-tube with diluted sulphuric acid, loosely wrap some magnesium ribbon in a little bit of filter paper, put this into the tube, close the mouth of the tube with the thumb, and *at once* invert the tube in a basin containing diluted sulphuric acid. Gas soon begins to come off (when the acid has penetrated the paper); let the tube get filled with this gas, and then set fire to the gas as you did before. The result is the same as before.

The gas produced by the reaction of zinc with diluted sulphuric acid seems to be the same as the gas produced when iron, or magnesium, is used in place of zinc.

• Exact experiments have proved that the gas is the same.

D. Repeat experiment C, but use diluted hydrochloric acid (about three parts water to one part conc. acid). Note the results.

The gas produced by the interaction of zinc and diluted hydrochloric acid seems to be the same as the gas produced when iron, or magnesium, is used in place of zinc. Exact experiments have proved that the gas is the same.

Putting together the results of A, B, C, and D, of this experiment, you seem justified in concluding, provisionally, that the gas produced when zinc reacts with diluted sulphuric acid is the same as the gas which is given off when iron, or magnesium, reacts with that acid; and that the same gas is formed when any one of these metals interacts with diluted sulphuric acid.

Extended and exact observations have justified this conclusion.

E. We shall now prepare on a larger scale the gas produced by the reaction of zinc, magnesium, or iron with diluted sulphuric

or hydrochloric acid, and make ourselves acquainted with some of its properties. It will be convenient to prepare the gas by the interaction of zinc and diluted sulphuric acid.

Arrange an apparatus as shown in figure 19 ; let the flask A be about 250 c.c. (about 8 oz.) capacity. Put water into the earthen

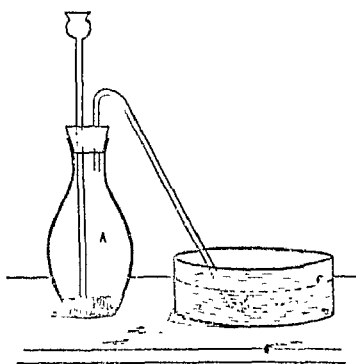


FIG. 19

ware trough used in collecting oxygen ; fill with water three thin glass jars like those used in the experiments with oxygen, and invert them in the water in the trough. Pour several test-tubeful of water into the flask, then incline it to one side and slip into it, cautiously, about 20 grams (say half a test-tubeful) of granulated zinc ; put the cork with its tubes into the flask, and pour diluted sulphuric

acid (about ten parts water to one part conc. acid) through the funnel tube, a little at a time, until after shaking and waiting for a few moments gas is given off pretty freely. When gas has been coming off for some minutes bring the end of the delivery tube under the water in the earthenware trough, and hold a test-tube filled with water over the delivery tube ; as soon as the test-tube is filled with the gas slip the thumb over the mouth of the tube, and bring it, mouth downwards, close to a lighted Bunsen lamp, and remove the thumb. If the gas in the tube ignites with a slight explosion, air is still coming off along with the inflammable gas ; in this case allow the action to proceed for a minute or two, then collect another tubeful of gas and test it as before. If the gas in the tube now ignites without any explosion, the inflammable gas is free from air.

You must not fill the jars with the gas until the whole of the air has been driven out of the apparatus. *A mixture of air and this inflammable gas is explosive and very dangerous :* for this reason you must take care not to bring a flame near the apparatus while you are making the gas.

When the gas that comes off is quite free from air fill the three jars with it; and as each is filled slip a small earthenware tray under its mouth, and lift the jar, standing mouth downwards in a little water in the tray, out of the earthenware trough (see figure 20). The water in the tray cuts off communication between the gas in the jar and the outer air, and prevents the gas escaping from the jar.

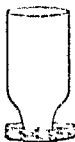


FIG. 20

Light a taper; remove one of the jars of the inflammable gas from its tray, and, *keeping the jar mouth downwards*, bring the lighted taper near the mouth of the jar. The gas takes fire, and burns quietly with a very slightly luminous flame. Light the taper at the burning gas, and then push the lighted taper into the jar; the taper goes out. Notice that the gas continues to burn for some little time at the mouth of the jar.

Turn one of the jars of gas mouth upwards, and *at once* bring a lighted taper near the mouth of the jar; the gas burns, but the flame goes out in a shorter time than the flame of the gas which was burnt in the jar held mouth downwards.

The results of these burnings make it probable that the gas you are dealing with is lighter than air. Perform an experiment with the third jar of the gas to try whether this is so or not. Hold mouth downwards, in the left hand, a thin jar rather smaller than one of those in which you have collected the gas; take the third jar of the gas, mouth downwards, in the right hand, and bring it alongside of, and a little lower than, the smaller jar which is full of air; now slowly depress the bottom of the jar of the gas, keeping the two jars in the positions you would place them in if you were pouring something from the lower jar (that containing the gas) into the upper (see figure 21). Hold the jars in this position for about a minute; then set the jar which contained the inflammable gas at the beginning of the experiment mouth downwards in one of the small trays. Bring a lighted taper to the mouth of the other jar, still held inverted in the hand; there is a slight explosion, and you notice a pale

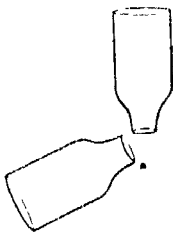


FIG. 21

nearly non-luminous flame playing round the mouth of the jar. Bring the taper into the other jar from which you have poured the inflammable gas; the taper burns quietly as it does in air; the whole of the inflammable gas has passed out of this jar.

The behaviour of this gas towards a burning taper is very different from that of oxygen.

Now write out a clear account of the preparation of oxygen from potassium chlorate, and the preparation of the inflammable gas from zinc and diluted sulphuric acid; and contrast the behaviours of the two gases towards a lighted taper.

LESSON X

EXAMINATION OF THE GAS PRODUCED BY DISSOLVING IRON, ZINC, OR MAGNESIUM IN DILUTED HYDROCHLORIC OR SULPHURIC ACID—*continued*. METHODS OF INVESTIGATING CHEMICAL CHANGES

Apparatus and materials required.—Flask, about 8 oz., used in last experiment. Small clean dry flask, about 2 oz. Pieces of ordinary glass tubing; piece of hard tubing about 6 inches long and $\frac{1}{2}$ to $\frac{3}{4}$ inch diameter; piece of soft tubing about $\frac{3}{4}$ inch diameter and 18 inches long. U-tube about 6 inches long and $\frac{1}{2}$ to $\frac{3}{4}$ inch diameter. A few good corks, and a few dry test-tubes. Files. Dish to contain water. Glass wool, or soft asbestos. Dry calcium chloride. Granulated zinc. Diluted sulphuric acid. Dry red lead. A little bit of lead. Pieces of white paper. Thermometer.

Experiment I.—*What is produced when the gas you are examining is burnt?*

You have found that the gas produced by the interaction of zinc and diluted sulphuric acid burns in air; you have now to discover what is produced in this burning. If the chemical change that occurs when the gas burns in air is similar to the changes that take place when lead and phosphorus are burnt, and when iron rusts, in air, then you would expect the product of the burning of this gas to be a compound (or compounds) of the gas with the oxygen of the air.

It is evident that the gas produced by the reaction of zinc and diluted sulphuric acid must be wet; before burning the gas, with the object of finding out what is produced, the gas ought to be dried. The solid compound called calcium chloride has the property of eagerly absorbing and combining with water;

if a stream of a wet gas, which gas is without action on calcium chloride, is passed rather slowly through a considerable quantity of that compound, the moisture is retained by the calcium chloride and the gas is dried.

Remove the cork from the flask used in part E of *Experiment II., Lesson IX.*, put a little more granulated zinc and some more diluted sulphuric acid into the flask, and fit into it a

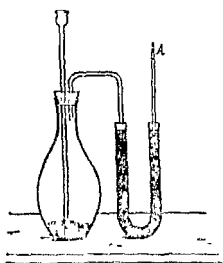


FIG. 22

caoutchouc cork carrying a funnel tube, and a short exit-tube connected with a U-tube—about 150 mm. (6 inches) long and 12 to 18 mm. ($\frac{1}{2}$ to $\frac{3}{4}$ inch) diameter, and containing small pieces of dry calcium chloride loosely packed in the tube with a little cotton wool between the calcium chloride and the corks of the tube (see figure 22). The cork in that end of the U-tube which is furthest from the flask must be fitted with a straight piece of glass tubing, about 100 mm. (4 inches) long, the upper end of which is narrowed to about 1½ mm. ($\frac{1}{16}$ inch) diameter (see A in figure 22).

After some minutes—say five minutes or so—place a test-tube mouth downwards over the narrowed tube from which the gas is issuing; *very slowly* move the test-tube upwards, and as soon as the end of the tube is above the open end of the exit-tube for the gas *at once* bring the test-tube, mouth downwards, to a Bunsen flame: if the gas in the test-tube takes fire quietly all the air is out of the apparatus; but if the gas ignites with a slight explosion the gas that is coming off is still mixed with air. *Repeat this test for the absence of air until you are quite sure that air-free gas is issuing from the apparatus*; then light the gas as it issues from the narrowed tube.

You must on no account bring a light near the apparatus until you have made certain that the whole of the air has been driven out.

Place over the burning gas the shorter end of a piece of glass tubing bent as shown in figure 23, and held in a clamp. This piece of tubing should be about 450 mm. (about 18 inches) long

and 15 mm. ($\frac{5}{8}$ inch) diameter. Drops of a colourless liquid soon form in the tube and fall into a clean dry test-tube placed as shown in the figure. When you have collected about an eighth of a test-tubeful of this liquid remove the bent tube, and blow out the flame. The liquid you have collected is colourless, it has no smell and no taste; it seems to be water. A definite property of water is that it boils at 100° C. under the ordinary atmospheric pressure. If the colourless, odourless, liquid produced by burning the inflammable gas in air boils at this temperature, that liquid is water.

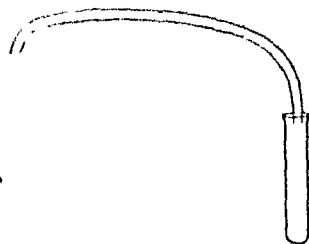


FIG. 23

Cautiously fit into the test-tube that contains the liquid a good cork, bored with a hole for the escape of vapour, and also carrying a thermometer the bulb of which reaches about half way down the tube. Support the tube in a clamp; and heat the liquid in the tube, by a *very small flame*, until it boils. Notice the thermometer; the mercury rises until it reaches 100° and then remains steady.

This experiment proves that water is formed when the gas produced by the interaction of zinc and diluted sulphuric acid is burnt in air after it has been dried.

The gas you have been examining is called *hydrogen*, because water is produced when it is burnt.

Some substance, or substances, besides water may be produced when hydrogen is burnt in air; what quantitative experiments would be needed to prove that water is the only product of the burning of dry hydrogen in air?

Experiment II.—*Is the water that is produced when hydrogen burns in air formed by the union of the hydrogen with oxygen in the air?*

You found in the last experiment that water is formed when hydrogen burns in air. Former experiments on burnings in air showed that burning phosphorus and strongly heated lead com-

bine with oxygen in the air, and that a similar change occurs when iron rusts in air. The products of these changes are compounds of oxygen with the element that is burnt (phosphorus, lead, and iron are elements); hence it is probable, for hydrogen also is an element, that water, which is produced when hydrogen burns in air, is a compound of hydrogen and oxygen. The object of the experiment now to be performed is to examine this probability.

Before beginning the experiment you must accept the accuracy of the statement that red lead, which is made by heating lead in air for a long time, is a compound of lead and oxygen only (compare *Experiments II. and III., Lesson V.*).

Arrange an apparatus as shown in figure 24. The flask A, and the U-tube B, are those that were employed in the last experiment; the U-tube is

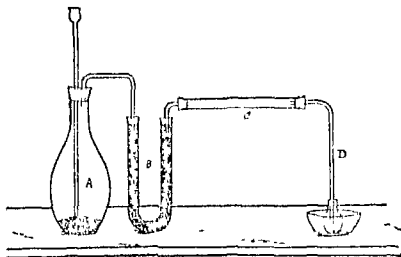


FIG. 24

connected by a short piece of glass tubing with a piece of hard glass tubing, C, about 150 mm. (6 inches) long and 12 to 18 mm. ($\frac{1}{2}$ to $\frac{3}{4}$ inch) diameter; the other end of this tube of hard glass is fitted with a good cork carrying a piece of glass

tubing about 220 mm. (9 inches) long, bent downwards as shown in the figure (D), and dipping into a small flask, which must be clean and dry; this flask stands in a vessel which contains cold water.

Remove the piece of hard tubing, C; push a small quantity of soft asbestos, or glass wool, which has been dried immediately before use by heating it strongly, a little way into the tube; then

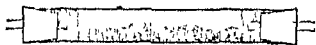


FIG. 25

put in enough dry red lead to fill the tube to about one-half (do not pack the red lead tightly), and follow this by a loose plug of dried

asbestos or glass wool. By tapping the tube gently cause the red lead to spread out, so that the hydrogen will have no difficulty

in passing through the tube. The tube has now the appearance shown in figure 25.

Fit the tube containing the red lead into its place in the apparatus; put granulated zinc into the flask A, and pour diluted sulphuric acid (one part conc. acid to ten parts water) down the funnel tube. After hydrogen has been passing through the apparatus for five minutes or so turn the tube D upwards, and test the issuing hydrogen to see that it is free from air, as directed in the last experiment. When hydrogen is coming off quite free from air, *but not till then*, turn the tube D downwards into the small flask, and begin to heat the tube which contains the red lead; heat very gently, moving the flame from end to end of the tube, sometimes allowing the flame to play on one part of the tube for a moment or two, and again moving it about around the whole tube. *Gradually* raise the temperature of the tube until a length of at least three inches of it is at a red heat. *If the heating of this tube is not done very gradually the glass will crack.* See that hydrogen is coming off in a fairly rapid stream; and keep the stream of hydrogen going, and the tube red hot, for *about twenty minutes*, or until at least about an eighth of a test-tubeful of a colourless liquid has collected in the little flask. Now remove the Bunsen lamp, *but do not take the apparatus to pieces until it is cold.*

Prove that the colourless, odourless, liquid that has collected in the flask is water, by determining its boiling-point, as directed in *Experiment I, of this Lesson* (p. 19).

When the apparatus is cold remove the tube containing the red lead; shake out its contents on to a piece of paper, and examine carefully what is on the paper; you notice some small, lustrous, metal-like, particles among the red lead. Pick out a few of these particles, and draw one of them across a piece of white paper; a mark is left on the paper. Press a few of the particles in a mortar with a pestle; they are easily flattened out. Draw a piece of lead across white paper, and press the lead in a mortar with a pestle; the lead behaves as the metal-like particles did.

Lead and water have been produced by heating red lead in dry hydrogen.

The results of this experiment show that water is a compound of hydrogen and oxygen (red lead is assumed to be a compound of lead and oxygen); and the results confirm the conclusion pointed to by Experiment I. of this Lesson, that the water produced by burning hydrogen in air is formed by the combination of the hydrogen with oxygen which is in the surrounding air.

Assuming that the only reaction which occurs when hydrogen is passed over heated red lead (lead oxide) is the formation of water (by the union of the hydrogen with the oxygen of the red lead), how would you propose to make use of this reaction for determining the weights of hydrogen and oxygen which combine to produce a determinate weight of water?

Note I.—It would be advisable to demonstrate that hydrogen and oxygen are obtained by passing an electric current through water mixed with some sulphuric acid, and to explain the methods and the reasoning whereby modifications of this experiment prove that water is composed of hydrogen and oxygen only.

Note II.—If time permits it is advisable that the student should heat (i.) iron oxide, and (ii.) copper oxide, in a stream of dry hydrogen, as directed in the experiment with red lead, noting the results, and comparing them with those obtained by heating red lead (lead oxide) in dry hydrogen. If there is not time for this, then it would be well to demonstrate the reactions of heated iron and copper oxides with dry hydrogen.

LESSON XI

PROPERTIES OF OXIDES

In Lesson VIII. you prepared four oxides, and you found that solutions in water of these oxides either turned blue litmus red, or red litmus blue. You have now to examine oxides belonging to these two classes—litmus-blueing oxides, and litmus-reddening oxides—with the object of finding out something about the changes which occur when an oxide of one kind reacts with an oxide of the other kind.

Apparatus and materials required.—Aqueous solutions of potassium oxide and sulphur trioxide. Sodium carbonate. Granulated zinc. Red and blue litmus solutions. Platinum wire. Sherry paper. Tapers. Pieces of calico. Piece of blue glass.

Experiment I.—*To examine the change that occurs when aqueous solutions of potassium oxide and sulphur trioxide are mixed in certain proportions.*

You are given solutions in water of *potassium oxide* and *sulphur trioxide*.

To a little of each solution in a test-tube add a few drops of blue litmus solution; then to other portions of the solutions of the two oxides add red litmus solution. Note the results. Add a little powdered sodium carbonate to separate portions of the solutions of the two oxides; if any gas is given off, after a little time bring a lighted taper near the mouths of the tubes and note what occurs. Now add some thin pieces of zinc to separate portions of the two solutions; if any gas is given off bring a lighted taper near the mouths of the tubes and note the results.

Place a couple of test-tubesful of the solution of sulphur trioxide in a basin, add six or eight drops (not more) of litmus solution, and then *slowly* pour in the solution of potassium oxide,

stirring constantly, until the red colour of the litmus becomes slightly less red. When this point is reached dilute some of the potassium oxide solution with several times its volume of water, dip a glass rod into this diluted solution, and transfer a drop of it to the basin, and stir; proceed in this way until the colour of the liquid in the basin is bluish purple, then set the basin on wire gauze over a Bunsen lamp and evaporate until froth forms freely on the surface of the liquid; now lower the flame, making it as small as you can, and stir the contents of the basin until almost the whole of the liquid has disappeared and a pasty solid is left, *but stop the evaporation before the solid becomes quite dry*. Remove this solid by means of a spatula to a piece of clean calico, and press until the solid is dry. Now dissolve the solid in water (the pressing in calico is to remove any liquid adhering to the solid, so that you may be sure that the reactions which you notice are reactions of the solid you have prepared, and not of something else), and to a small quantity of this solution add a drop or two of blue litmus solution and note the result. To another small quantity of the solution of the solid add a few drops of red litmus solution and note the effect. To two other portions of the solution of the solid add a few pieces of zinc and a little sodium carbonate, respectively, observe carefully if any visible change takes place, and note what you see.

Now clean a piece of platinum wire, by rubbing the wire with emery paper, dipping it into some concentrated hydrochloric acid in a test-tube (*do not dip the wire into the bottle of acid on the shelf*), heating it in a Bunsen flame, again dipping into the acid and heating in the flame, and proceeding thus until the wire does not impart the slightest colour to the non-luminous flame. When the wire is clean dip it into the solution of the solid and then bring the wire into the non-luminous flame of the Bunsen lamp; the flame acquires a slight and transient purplish lavender colour, which appears redder when looked at through a piece of blue glass. Clean the wire again, dip it into the solution of sulphur trioxide, and then bring it into the flame; the flame is not coloured.

Having cleaned the wire once more, dip it into the solution of potassium oxide and bring it into the flame; the flame is

slightly coloured purplish lavender, and the colour looks redder when the flame is viewed through blue glass.

Pour into a test-tube a little of the solution of the solid obtained by mixing the solutions of the two oxides and evaporating, and add a little diluted hydrochloric acid, and then a few drops of a solution of barium nitrate: a white solid forms in the liquid. Perform this reaction with barium nitrate, preceded by addition of hydrochloric acid, first with the solution of sulphur trioxide, and then with the solution of potassium oxide, and note the results.

The following tabular arrangement presents the results of these experiments.

	<i>Litmus solution</i>	<i>Sodium carbonate</i>	<i>Zinc</i>
Potassium oxide solution. Sulphur trioxide solution.	Red to blue. Blue to red.	No visible change. Colourless gas produced, which jets out taper.	No visible change. A gas is produced which takes fire.
Solution of the solid formed by mixing definite quantities of the two oxides and evaporating.	No effect on either blue or red.	No visible change.	No visible change.
	<i>Non-luminous flame</i>	<i>Barium nitrate, preceded by hydrochloric acid</i>	
Potassium oxide solution. Sulphur trioxide solution. Solution of the solid formed by mixing definite quantities of the two oxides and evaporating.	Coloured purplish lavender. No visible effect. Coloured purplish lavender.	No visible change.	White solid formed. White solid formed.

These experiments show that certain properties of sulphur trioxide, and certain properties of potassium oxide, disappear when definite quantities of solutions in water of these two oxides are mixed. For, on evaporating the mixture of the two solutions, a solid is obtained an aqueous solution of which has no effect on the colour of either blue or red litmus, and does not react visibly either with sodium carbonate or with zinc: whereas a solution in water, of sulphur trioxide turns blue litmus red, reacts with sodium carbonate to produce a gas which may be

Carbon dioxide, and reacts with zinc to produce a gas which is probably hydrogen; and a solution in water of potassium oxide turns red litmus blue, but has no visible action on either sodium carbonate or zinc.

The experiments also show that the solid formed by mixing definite quantities of solutions of the two oxides, and evaporating, has at least one property in common with potassium oxide, and at least one property in common with sulphur trioxide; for both potassium oxide and the solid in question impart a purplish lavender colour to a non-luminous flame (sulphur trioxide does not do this); and both sulphur trioxide and the solid in question, when dissolved in water, give a white precipitate with barium nitrate, which precipitate is insoluble in hydrochloric acid (potassium oxide does not do this).

The litmus-blueing oxide—potassium oxide—is a representative of a large class of oxides which are called *basic oxides*. The litmus-reddening oxide—sulphur trioxide—is a representative of a large class of oxides which are called *acidic oxides*. The compound formed by the reaction of definite quantities of these two oxides—potassium sulphate—is a representative of a large class of compounds which are called *salts*.

All compounds of the element potassium colour a hot non-luminous flame purplish violet; this reaction is not characteristic of potassium oxide or potassium sulphate, but it is used as a test for detecting any compound of potassium. Sulphuric acid (a solution in water of sulphur trioxide contains sulphuric acid), or any of those compounds derived from this acid which are called sulphates, gives a white precipitate with barium nitrate, which precipitate is insoluble in hydrochloric acid; this reaction is not characteristic of a solution of sulphur trioxide or of potassium sulphate, but it is used as a test for detecting any sulphate. We shall find hereafter that a great part of qualitative analysis rests on facts of this kind; we shall find that many compounds of each element, or of each one of certain compound-groups of elements, have some common reactions by the application of which that element, or group of elements, can be detected even when it is combined with other elements.

LESSON XII

PROPERTIES OF OXIDES - *continued*

Apparatus and materials required.—Zinc oxide that has been strongly heated. Red and blue litmus solutions. Solution in water of sulphur trioxide. Sodium carbonate. Granulated zinc. Platinum wire. Emery paper.

Experiment I.—*To examine the change which occurs when zinc oxide dissolves in an aqueous solution of sulphur trioxide.*

Shake a little powdered zinc oxide with water for a few minutes,¹ and test the water with blue and red litmus solutions, separately; the colour of the blue litmus is not changed, the red litmus may become slightly purple in colour.

If zinc oxide dissolves in water the solution hardly affects the colour of litmus.

Pour into a basin two or three test-tubesful of a solution in water of sulphur trioxide, and heat for a minute or two; then shake in powdered zinc oxide, a little at a time, stirring constantly, and boiling the liquid after each addition of zinc oxide. You notice that the zinc oxide slowly dissolves. Proceed in this way until some zinc oxide remains undissolved when the oxide has been in the boiling liquid for several minutes; then pour about a couple of test-tubesful of water into the basin, heat for a minute or two, and run the liquid through a filter, allowing the filtrate to drop into a small basin. Evaporate the filtrate over a *low flame* until a crust begins to form on the surface of the liquid; then set the basin aside until it is cold.

When the liquid is cold pour it off from the solid that has

¹ The zinc oxide should be heated by a foot blow-pipe for some time before use, as specimens of this compound often contain zinc carbonate

separated from it; then remove the solid to a piece of calico and press till dry.

When you have finished the experiment try to find a reason for the direction to press this solid till it is dry.

Dissolve most of the dried solid in water (*keep a little of it*), and examine the action of this solution on (i.) red litmus, (ii.) blue litmus, (iii.) sodium carbonate, (iv.) zinc, (v.) barium nitrate, solution followed by hydrochloric acid. Write out your results in the tabular form shown at the end of *Experiment I. of last Lesson*; and contrast them with the reactions of sulphur trioxide solution on litmus and on the other substances just mentioned.

The experiments you have made show that most of the properties of the solution of sulphur trioxide have been removed by the solution in it of zinc oxide, followed by evaporation; but that the reaction with barium nitrate and hydrochloric acid is common to solutions of sulphur trioxide and of the solid obtained by saturating a solution of that oxide with zinc oxide and evaporating.

From the conditions of the preparation of the solid obtained in this experiment it is almost certain that zinc must enter into the composition of that substance; in other words, that the solid must be a compound of zinc. But it is advisable to show experimentally that that solid substance has some property in common with a body which is known to be a compound of zinc. For this purpose make a little loop on the end of a *clean* platinum wire (see *Experiment I. of last Lesson*, p. 54, for the method of cleaning a platinum wire), take a *very small* quantity of zinc oxide on to this loop, heat for a few moments in the Bunsen flame, then let one drop of a solution of cobalt nitrate fall on to the solid, and heat again *for a minute or two*; when the solid is cold it is seen to be green. This reaction is characteristic of zinc compounds. Clean the platinum wire, and repeat the reaction, using a *very little* of the solid obtained by saturating sulphur trioxide solution with zinc oxide and evaporating. The visible result is the same as with zinc oxide.

Although zinc oxide does not react with water and litmus in the same way as potassium oxide (see *Experiment I. of last*

Lasson), nevertheless zinc oxide is a basic oxide; it reacts with sulphur trioxide, which is an acidic oxide, and the product is a salt—zinc sulphate—that does not exhibit the characteristic reactions of the acidic oxide from which it has been produced.

The distinction should be clearly grasped between the typical reactions of acidic oxides and the characteristic reactions of this or that individual acidic oxide; also between the typical reactions of basic oxides and the characteristic reactions of any individual basic oxide. The typical reactions of acidic oxides soluble in water are that aqueous solutions of these oxides turn blue litmus red, react with sodium carbonate (and many other carbonates) giving off carbon dioxide, react with zinc (and many other metals) to give off gas (which is generally hydrogen); all acidic oxides combine with basic oxides to form salts. The typical reaction of basic oxides is that they react with acidic oxides to produce salts. Subsequent experiments will make clearer the terms *acidic oxide*, *basic oxide*, and *salt*.

LESSON XIII

EXERCISES ON THE DETERMINATION OF THE BASIC OR ACIDIC
CHARACTERS OF OXIDES

You are given four oxides, *A*, *B*, *C*, and *D*; and you are asked to make experiments with these, and from the results of your experiments to classify the oxides as basic or acidic. The oxides *A*, *C*, and *D* are solids; the oxide *B* is given in solution in water.

If an aqueous solution of an oxide, which is known to be either a basic or an acidic oxide, changes the colour of red litmus to blue, and does not react visibly with zinc or with sodium carbonate, the oxide is basic; such an oxide will combine with some acidic oxide to form a salt. But an oxide, when shaken with water, may have no effect on the colour of litmus, and may yet be a basic oxide. The one reaction common to all basic oxides is that they combine with acidic oxides to form salts.

If an aqueous solution of an oxide, which is known to be either a basic or an acidic oxide, changes the colour of blue litmus to red, and reacts with zinc and with sodium carbonate, to give off a gas in each case, the oxide is acidic; such an oxide will combine with some basic oxide to form a salt. But an oxide, when shaken with water, may have no effect on the colour of litmus, and may yet be an acidic oxide. The one reaction common to all acidic oxides is that they combine with basic oxides to form salts.

You know that potassium oxide is a basic oxide, and that sulphur trioxide is an acidic oxide (*Lessons XI. and XII.*). If you find that a certain oxide, which you are told is either basic or acidic, combines with potassium oxide, then the oxide in question is acidic. If you find that a certain oxide, which you are told is either basic or acidic, combines with sulphur trioxide, then the oxide in question is basic.

All the salts formed by the combination of potassium oxide with acidic oxides impart a lavender-violet colour to a hot non-luminous flame; this reaction enables you to recognise these salts.

A solution of any one of the salts formed by the combination of sulphur trioxide with a basic oxide reacts with a solution of barium nitrate to form a white precipitate which is not dissolved by diluted hydrochloric acid; this reaction enables you to recognise these salts, which are called *sulphates*.

To determine the basic or acidic character of an oxide known to be basic or acidic.

I. Shake a *little* with distilled water; and note the effect of the liquid (*a*) on litmus, (*b*) on zinc, and (*c*) on sodium carbonate.

II. If the results of I. indicate the oxide to be basic, proceed to prove that it combines with the acidic sulphur trioxide. If the results of I. indicate the oxide to be acidic, proceed to prove that it combines with the basic potassium oxide.

If the oxide dissolves in water, to an aqueous solution of it add a solution either of sulphur trioxide (that is, add diluted sulphuric acid), or of potassium oxide (that is, add diluted potash solution), as the case may be, till the liquid is neutral to litmus; then evaporate towards dryness, press in *calico* till quite dry the solid that forms as the evaporated liquid cools, and prove that the salt thus obtained is a compound either of potassium oxide, or of sulphur trioxide, accordingly as you neutralised by a solution of the former or of the latter of these oxides.

If the oxide does not dissolve in water, saturate a hot solution of sulphur trioxide (diluted sulphuric acid), or of potassium oxide (diluted potash solution), as the case may be, with the oxide -- as directed in *Lesson XII.* (p. 57)—evaporate towards dryness, press in *calico* till quite dry the solid that forms as the evaporated liquid cools, and prove that the salt thus obtained is a compound either of sulphur trioxide, or of potassium oxide, accordingly as you saturated a solution of the former or of the latter of these oxides with the oxide under examination.

NOTE.—If the effect of a coloured solution on litmus is to be examined, it is better to dip pieces of paper coloured with blue and red litmus into the solution.

To make the method of procedure quite clear the results of determinations of the basic or acidic characters of two oxides are appended. Write out the results of your experiments in this form.

I.	II.	III.
<i>Oxide X</i> .—Solid; dissolved fairly easily in water.	Solution turned blue <i>litmus</i> red; reacted with <i>sodium carbonate</i> , giving off a gas which put out a lighted taper; and reacted with <i>zinc</i> to produce a gas which took fire. This suggests that <i>oxide X</i> is acidic; if <i>X</i> is acidic it will combine with potassium oxide, which is a basic oxide (Col. III.)	To solution added <i>litmus</i> , and then solution of <i>potassium oxide</i> till liquid was neutral colour; evaporated towards dryness; pressed solid that separated on cooling till dry, and then dissolved it in water. This solution turned red <i>litmus</i> slightly blue; it gave the <i>flame reaction</i> for compounds of potassium; and it had no visible reaction with either <i>sodium carbonate</i> or <i>zinc</i> .

Oxide X is acidic: because an aqueous solution of it turns blue *litmus* red, and reacts with a basic oxide, namely potassium oxide, to form a compound which has not the characteristic properties of the original oxide *X*.

I.	II.	III.
<i>Oxide S</i> .—Solid; did not dissolve in water.	When shaken with water did not affect colour of <i>litmus</i> , nor give off gas from <i>sodium carbonate</i> or <i>zinc</i> . <i>Oxide S</i> is probably basic; if it is it will combine with sulphur trioxide, which is an acidic oxide (Col. III.)	To solution of <i>sulphur trioxide</i> added <i>S</i> , warmed, added more of <i>S</i> , and so on till a little of <i>S</i> remained undissolved; filtered and evaporated solution towards dryness; dried solid that separated on cooling, and then dissolved it in water. This solution was neutral to <i>litmus</i> ; it had no visible action on <i>sodium carbonate</i> or <i>zinc</i> ; and it gave the reaction with <i>barium nitrate</i> and <i>hydrochloric acid</i> characteristic of sulphates.

Oxide S is basic; because (although water shaken with it does not affect the colour of *litmus*) the oxide does not react with sodium carbonate or zinc, and it forms a compound with an acidic oxide, namely sulphur trioxide, which compound has not the characteristic properties either of the original oxide *S*, or of the acidic sulphur trioxide which was caused to combine with *S*.

LESSON XIV

THOSE ELEMENTS WHOSE OXIDES ARE BASIC RESEMBLE COPPER, IRON, TIN, SILVER, LEAD, &c.; THEY ARE METALS. EXAMINATION OF INTERACTIONS OF METALS AND ACIDS

Apparatus and materials required.—Flask fitted like that used in making hydrogen in Lesson IX. Trough. Two thin gas jars. Two small trays. Granulated zinc. Granulated tin. Sodium carbonate. Litmus. Calico. Tapers. Clean platinum wire. Cobalt nitrate solution. Silver nitrate solution. Mercuric chloride solution.

In Lesson IX., Experiment II., you prepared hydrogen by the interaction of the metal zinc and diluted sulphuric acid. Most basic oxides (see Lessons XI. and XII.) are oxides of elements that resemble zinc in their chemical reactions. You have now to examine the reactions which occur between a few of the zinc-like elements and some of the common acids.

The commonest acids are *sulphuric* (oil of vitriol), *nitric* (*aqua fortis*), *hydrochloric* (spirits of salt, or muriatic acid), and *acetic* (the acid in vinegar). The ordinary metals are zinc-like elements; for instance *copper*, *tin*, *lead*, *iron*, *silver*, and *aluminium*.

In the present lesson you will examine some parts of the reaction between zinc and diluted sulphuric acid which were passed over in Lesson IX.; and you will make a partial examination of the interaction between tin and hydrochloric acid.

Experiment I.—To examine the solid obtained by dissolving zinc in diluted sulphuric acid and evaporating.

To three or four test-tubesful of diluted sulphuric acid in a basin add several small pieces of granulated zinc; allow the re-

action to proceed, warming *very slightly* if the reaction slackens much. You know some of the properties of the gas—hydrogen—which is given off in this reaction; you have now to find out what is formed in this chemical change besides hydrogen.

When all, or almost all, the zinc has dissolved, decant the liquid into another basin (filtering if necessary), evaporate over a *low flame* till a froth forms on the liquid, and then set aside the basin till it is cold (if the basin is floated in cold water the cooling process will be hastened). Pour off the cold liquid from the crystalline solid that has formed into another basin; evaporate this liquid *very slightly*, and set it aside to cool (*see forward*). Remove the crystalline solid from the basin to a piece of clean calico, and press it till *quite dry*; then dissolve the dry solid in the smallest possible quantity of warm water, evaporate slightly, and let cool. Pour away the cold liquid from above the crystals that have formed (if crystals have not formed evaporate a little further), dry the crystals by pressure in calico, and then dissolve most, *but not quite all*, of the dried solid in a little water.¹ Prove that a little of this solution gives the reaction with barium nitrate and hydrochloric acid which is characteristic of a sulphate (see p. 55); also prove that the solution is neutral to litmus, and also that it has no visible action on sodium carbonate or zinc (compare p. 58). Now heat an *extremely small quantity* of the dried solid, supported on a *small loop* of clean platinum wire, in a Bunsen flame, then moisten with a drop of cobalt nitrate solution, and heat again strongly for several moments; you obtain the reaction that is characteristic of compounds of zinc (see p. 58).

This experiment shows that when zinc dissolves in diluted sulphuric acid the zinc reacts with the acid to form a crystallisable solid, which gives a reaction characteristic of zinc compounds, and also a reaction characteristic of sulphates (that is, salts derived from sulphuric acid). You already know that hydrogen is also a product of the reaction between zinc and diluted sulphuric acid.

¹ The re-crystallisation from water is done for the purpose of removing any sulphuric acid that may have adhered to the crystals obtained by the first evaporation of the solution of zinc in sulphuric acid.

Now turn back to the basin wherein you evaporated the liquid poured off from the solid that was formed by boiling down the solution of zinc in diluted sulphuric acid. A white solid has separated from this liquid (if the liquid is free from solid matter evaporate a little further and let cool). Dry this solid *thoroughly*, by pressure in calico, and apply to it the same tests you applied to the first crop of crystals. So far as these qualitative tests can decide, the second crop of crystalline solid is the same compound as the first crop.

This experiment indicates—it does not, however, prove—that zinc sulphate is the only solid product of the reaction between zinc and diluted sulphuric acid, under the conditions of your experiment.

A comparison of this result with the results of *Experiment I. of Lesson XII.* makes it very probable that the same solid compound is produced by the interaction of zinc and diluted sulphuric acid as is formed when zinc oxide reacts with that acid.

Experiment II.—*To examine the interaction of tin and concentrated hydrochloric acid.*

Set up an apparatus like that used in making hydrogen, in *Experiment II., E.* of *Lesson IX.* (p. 44); but arrange the apparatus so that the flask can be heated on wire gauze over a Bunsen lamp. Put about half a test-tubeful of granulated tin into the flask; pour *concentrated* hydrochloric acid down the funnel tube, about a test-tubeful at a time, and warm. When gas has been coming off freely for a few minutes collect a test-tubeful of the gas, and bring the test-tube mouth downwards to a flame; if the gas burns quietly fill two thin glass jars with it, as you filled the jars with hydrogen in *Lesson IX., Experiment II., E.* Pour the acid and the undissolved tin from the flask into a basin; set this over a low flame in a draught place, and allow the reaction to proceed (*see forward*, p. 66).

Lift one of the jars with its mouth downwards from the water in the trough, and *at once* bring a lighted taper to the mouth of the jar: note the result. Place the other jar mouth

upwards on the bench, and after a minute bring a lighted taper to the mouth of the jar, and note what occurs.

The results of these two experiments show that the colourless gas produced by warming concentrated hydrochloric acid with tin is very light, and that it takes fire easily and burns with a scarcely luminous flame. The gas is probably hydrogen.

Extended and exact examination has shown that this gas is hydrogen.

Recall the results of *Experiment II.*, C and D, *Lesson IX.*; you obtained hydrogen by the reaction of zinc, iron, or magnesium with either diluted sulphuric or hydrochloric acid.

Something besides hydrogen must surely have been formed in the reaction between tin and hydrochloric acid. To find out whether anything else has been produced, and if something has been formed to discover, if possible, what that something is, continue the evaporation of the liquid in the draught place—if all the tin has dissolved add a little more tin—until a white pasty mass is obtained; *the evaporation must be done over a very low flame, and you must stir vigorously when the liquid has begun to get somewhat thick.* Dry this pasty solid as thoroughly as you can by pressing it repeatedly in calico; and then dissolve the dried solid in water. To a portion of this solution add a few drops of nitric acid, and then a little silver nitrate solution; a white curdy precipitate forms, which darkens in colour after being exposed to the sunlight for a little time. To another portion of the solution add a few drops of mercuric chloride solution; a white precipitate forms, which very soon becomes grey and then nearly black.

Now dissolve a small piece of tin foil in a little warm concentrated hydrochloric acid. To this solution add a little water, and then a few drops of mercuric chloride solution; a white precipitate is formed, and this precipitate soon turns grey and then nearly black. As the liquid to which you have added mercuric chloride solution was prepared by dissolving tin in hydrochloric acid, you seem justified in concluding that the reaction with mercuric chloride solution must be a reaction

either of tin or of hydrochloric acid: to a little diluted hydrochloric acid add some mercuric chloride solution, no visible change occurs; therefore the formation of a white precipitate, which rapidly darkens in colour, on addition of mercuric chloride solution to a liquid, is very probably a reaction of tin in solution. More extended investigation has justified this conclusion, with a proviso which need not be insisted on here.

The solid which you obtained by dissolving tin in hydrochloric acid and evaporating was, therefore, a compound of tin.

To a little diluted hydrochloric acid add a few drops of silver nitrate solution; a white curdy precipitate is obtained, which darkens on standing in the sunlight. This is a characteristic reaction of hydrochloric acid and of salts obtained from this acid; these salts are called *chlorides*.

The solid which you obtained by dissolving tin in hydrochloric acid and evaporating was, therefore, a compound derived from hydrochloric acid.

It appears, then, that in the reaction of tin with hydrochloric acid, hydrogen and a salt composed of tin and hydrochloric acid, or of tin and some constituent of hydrochloric acid, are produced.

Your experiments do not determine whether there are, or are not, other products of the interaction of tin and hydrochloric acid.

LESSON XV

INTERACTIONS OF METALS AND ACIDS—*continued*

Apparatus and materials required.—Flask, with cork carrying funnel-tube and exit-tube, to collect gas over water. Trough. Three jars for collecting gas; three small trays. Copper turnings or clippings. Thin cardboard. Red phosphorus. Deflagrating spoon. Powdered ferrous sulphate. Tapers. Slips of wood.

Experiment I.—*To examine the reaction between copper and nitric acid.*

Set up the apparatus used in *Experiment II.* of last Lesson for examining the reaction of tin with conc. hydrochloric acid. Put about a test-tubeful of copper turnings, or clippings, in the flask; cover the copper with water, and then pour diluted nitric acid (about equal parts concentrated acid and water) down the funnel tube, a little at a time, with frequent shaking, until a visible reaction begins and gas is given off. The colour of the gas in the flask is reddish brown; the gas, therefore, is not hydrogen, although hydrogen *may* be present mixed with some other, coloured, gas.

Allow the gas to bubble through the water in the trough for a little. Notice that the gas in the flask gradually becomes lighter in colour, and that after some minutes it is colourless; but that the bubbles of gas escaping from the surface of the water are coloured reddish brown in the air.

Now fill three jars with the gas, in the usual way. Have ready a taper that will burn with a *small* flame, and a smouldering chip of wood. Bring the chip of wood into one of the jars held mouth upwards; the smouldering flame is extinguished: *at once* plunge the lighted taper into the same jar of gas; the taper goes out. Put a little red phosphorus into a clean defla-

grating spoon, set fire to the phosphorus, and *when it is burning brightly* plunge the spoon into another jar of the gas; the phosphorus continues to burn.

If you looked attentively at the gas in the jars as you were performing these experiments you noticed that as soon as each jar was turned mouth upwards the colourless gas in it became reddish brown. Turn the third jar of the gas mouth upwards and let it stand for a few moments; then cover the mouth with a piece of cardboard, bring the jar mouth downwards under the water in the trough, withdraw the cardboard, and shake the jar. The water rises in the jar. Now, considering that the jars filled with the colourless gas stood with their mouths under water for some little time without the water rising in the jars, this part of the experiment proves that the reddish gas produced by exposing the colourless gas to air is decidedly more soluble in water than the colourless gas. The colourless gas is called *nitric oxide*, and the reddish gas *nitrogen dioxide* (sometimes *nitrogen tetroxide*); you will have to deal with these gases again when you are examining the properties of nitric acid.

So far as these experiments have gone they have not indicated the existence of hydrogen among the products of the reaction of nitric acid and copper.

Now turn to the contents of the flask. Pour off the liquid from the undissolved copper into a basin, evaporate this liquid, *over a low flame* in draught place, until it begins to get slightly thick, and then cool it by floating the basin in cold water. Pour off the liquid from the blue crystals that have formed (*keep this liquid*); dry the crystals *thoroughly* by pressing in calico, and re-crystallise the solid from water (see p. 64).

Reasoning from the results of the experiments in the last lesson, you would expect these crystals to be composed of copper, and nitric acid or some constituent of nitric acid.

Now the liquid poured off from the crystals must contain both copper and nitric acid; you may therefore make use of this liquid to determine some characteristic reaction of each of these substances.

To a little of this liquid add ammonia solution until the smell of ammonia is apparent after thoroughly shaking the

liquid; the liquid becomes deep azure blue in colour. This reaction with ammonia is characteristic of copper, and compounds of copper, in solution.

Mix another small portion of the liquid poured off from the blue crystals with about its own bulk of *concentrated* sulphuric acid; take very great care to pour the acid in slowly while you hold the mouth of the tube away from yourself, and perform the mixing by pouring from one tube to another, not by putting your thumb on the mouth of the tube and shaking.

CONCENTRATED SULPHURIC ACID BURNS THE FLESH HORRIBLY.

Now run cold water on to the outside of the tube containing the mixture of the blue liquid and sulphuric acid, until the tube and its contents are quite cold; then dissolve a little powdered ferrous sulphate in cold water in a test-tube (do not heat, and then cool), and pour this solution *very slowly* down the tube containing the liquid mixed with sulphuric acid, while you hold the tubes as shown in figure 26. The comparatively light solu-

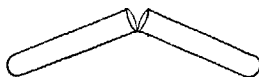


FIG. 26.

tion of ferrous sulphate floats on the surface of the liquid containing the comparatively heavy sulphuric acid, and you notice a brown colouration appearing where the two liquids meet. The production of this brown colouration under these conditions is a characteristic reaction of nitric acid, and of nitrates (which are salts derived from nitric acid).

You will return to this reaction when you are studying the properties of nitric acid.

Now apply these tests for copper and nitric acid to a solution in water of the blue crystals. The results show the crystals to be a compound of copper, and to be a compound of nitric acid.

Your experiments show that in the interaction of copper and nitric acid a colourless gas is produced, which changes in the air to a reddish gas; and that a salt composed of copper and nitric acid, or of copper and some constituent of nitric acid, is also formed. Your experiments do not

determine whether hydrogen is, or is not, also produced; but they do not directly indicate the presence of hydrogen among the products of the reaction.

Putting together the results of *Experiment II., Lesson IX.*, with those of the experiments performed in the last, and the present, lesson, you have found that hydrogen is produced in the interaction between diluted sulphuric acid and any one of the three metals, zinc, iron, or magnesium; and that hydrogen is also produced in the interaction between hydrochloric acid and the metal tin: also that a colourless, non-inflammable, gas, which is not hydrogen (although it may possibly be mixed with a little hydrogen), is produced by the interaction of nitric acid and the metal copper. You have also found that, besides the gaseous product (or products) of these reactions between acids and metals, there is formed in each case a compound of the metal and the acid, or it may be some constituent of the acid, employed.

LESSON XVI

EXAMINATION OF THE INTERACTIONS OF METALLIC OXIDES
AND ACIDS. PREPARATION OF SALTS

Apparatus and materials required.—Pure copper oxide. Litharge. Granulated lead. Alcohol. Silver nitrate solution.

In *Lessons VII. and VIII.*, and in part of *Lesson IX.*, you found that the atmosphere contains a gas which plays a very important part in many processes of combustion, inasmuch as this gas (oxygen) enters into chemical union with the burning body.

In the *second experiment of Lesson IX.* you discovered a gas quite unlike oxygen. You found that this gas (hydrogen) is produced when zinc, iron, and certain other metals, interact with diluted sulphuric or hydrochloric acid; *Experiment I. of Lesson XV.* taught you that the metal copper reacts with nitric acid to produce a gas which is not hydrogen, although your experiment did not conclusively prove the complete absence of hydrogen from the gaseous product of that reaction.

Experiments I. and II. of Lesson X. proved that water is produced when dry hydrogen burns in air, and that water is a compound of hydrogen and oxygen; that experiment (taken along with previous experiments) showed you that the chemical change which occurs when hydrogen burns in air is like the changes which take place when phosphorus burns in air, when lead is strongly heated in air, and when iron rusts in air.

In *Lessons XI. and XII.* you examined some of the reactions of certain oxides; you found that some oxides combine with one another to produce definite substances in which many of the properties of the combining oxides have disappeared. These definite substances formed by the interaction of *basic and acidic oxides* are called *salts*.

In the present lesson, and in some other lessons, you will be asked to examine the chemical properties of certain salts, chosen as representatives of this most important class of compounds.

The present lesson will be devoted to an examination of some of the reactions whereby salts are prepared. A comparison of the results of *Experiment I., Lesson XII.*, with those of *Experiment I., Lesson XIV.*, makes it probable that the salt obtained by the reaction of zinc with diluted sulphuric acid is the same as the salt obtained by the reaction of zinc oxide with diluted sulphuric acid. You know from *Experiment I. of Lesson XV.* that a greenish blue salt, which gives the reaction characteristic of copper, and also the reaction characteristic of nitric acid and a nitrate, is produced by dissolving the metal copper in nitric acid and evaporating the solution. If it is true that the same salt is produced by dissolving zinc oxide in diluted sulphuric acid as is formed by dissolving the metal zinc in that acid, then it is possible that a solution of copper oxide in nitric acid will yield the same salt, on evaporation, as is obtained by dissolving the metal copper in nitric acid and evaporating. You must now test this hypothesis by experiment. You will then be asked to compare the interaction of lead oxide and hydrochloric acid with the interaction of the same acid and the metal lead; and, finally, to compare these two reactions with the interactions of nitric acid and copper, and the same acid and copper oxide.

Experiment I.—*Is a salt produced by the reaction between nitric acid and copper oxide? If a salt is formed, is it the same salt as that which is produced by dissolving copper in nitric acid and evaporating?*

To three or four test-tubesful of diluted nitric acid (about three parts concentrated acid to one part water) heated in a basin, in a draught place, add pure powdered copper oxide, little by little, boiling for a minute or so after each addition of the oxide, until some of the oxide remains undissolved when you have boiled for a few minutes. Notice that gas is not given off during the solution of copper oxide in nitric acid; recall the fact that the process of dissolving copper in that acid was accompanied by the production of a gas. Run the greenish blue liquid through a filter

into a basin, and evaporate the filtrate, over a *low flame*, until crystals separate when you cool a little of the liquid in a test-tube; allow the liquid in the basin to get cold; pour off the liquid from the crystals that have formed; dry the crystals *thoroughly* by pressure in calico; dissolve the dry solid in water; and prove, that this solution gives the reaction with ammonia which is characteristic of copper, and the reaction with concentrated sulphuric acid and ferrous sulphate which is characteristic of nitric acid or a nitrate (see pp. 69, 70).

Copper oxide has reacted with diluted nitric acid to produce a nitrate of copper; and, as far as you can judge from your experiments, this salt seems to be the same as that produced in Lesson XV., Experiment I., by the reaction of copper with nitric acid.

Experiment II.—*Is a salt produced by the interaction of lead and hydrochloric acid?*

Put a small piece of granulated lead, or lead foil, into a test-tube, add some diluted hydrochloric acid, and boil for a minute or so, *in the draught place*; there is little or no visible change, at the most only a slight production of gas. Pour off the diluted hydrochloric acid, substitute concentrated hydrochloric acid, and boil for a few minutes *in the draught place*; the lead is evidently acted on by the acid, as bubbles of gas are seen coming from the surface of the metal, but the action is not rapid. After boiling for some minutes pour the liquid, *while boiling*, from the undissolved lead into a beaker; add a fresh quantity of concentrated hydrochloric acid to the lead, boil for some minutes, and pour the *boiling* liquid into the same beaker as before. Now add to the acid liquid in the beaker at least three times its own volume of cold water, and cool by placing the beaker in cold water. When quite cold pour off the liquid, as completely as you can, from the white, crystalline, solid that has separated; add *not more than a twentieth of a test-tubeful* of cold water to the solid; shake; let settle, and pour off the water. Repeat this washing with a *very little* cold water; the object is to remove any hydrochloric acid that may be adhering to the solid, so that you have only this crystalline solid to deal with in the next part

of the experiment.¹ Now pour about a test-tubeful of water on to the solid in the beaker, and boil; the white solid slowly dissolves in the boiling water (if the solid does not all dissolve after boiling for, say, five minutes, add a little more water and boil again). Cool the liquid; the solid is re-formed.²

The interaction of lead and boiling concentrated hydrochloric acid has produced a white, crystalline solid, which dissolves in boiling water, but crystallises again as the water cools.

From the analogy of the results of previous experiments on the solid products of the reactions of metals with acids, you would expect this white, crystalline solid to be a compound of lead with hydrochloric acid or some constituent of that acid.

Dissolve the white, crystalline solid in boiling water, and to a portion of this solution add two drops of diluted nitric acid and then a little silver nitrate solution; a white, curdy, precipitate forms, which darkens on exposure to sunlight. This reaction you know to be characteristic of chlorides (see p. 67).

To the other portion of the solution of the solid in boiling water add some alcohol and then a little diluted sulphuric acid; a white precipitate forms. Considering the conditions of formation of the crystalline solid, and considering you have proved that solid to be a chloride, this reaction with alcohol and diluted sulphuric acid must be due either to lead or to the other constituent, which we may call *the chloride constituent*, of the salt. Now add alcohol and diluted sulphuric acid to a little hydrochloric acid; no visible change occurs: the reaction with alcohol and sulphuric acid is not due to the chloride constituent of the salt. Dissolve a small piece of lead in hot diluted nitric acid—notice that a reddish gas is given off, and recall the fact that a reddish gas was produced during the reaction between the metal copper and nitric acid, in *Experiment I., Lesson XV.*—and to this solution add alcohol and diluted sulphuric acid; a white precipitate is produced. The reaction with alcohol and sulphuric acid is, therefore, due to lead. The white solid obtained

¹ The removal of the adhering liquid from the salts you prepared in former experiments was accomplished by pressing in calico.

² Notice the assumption that is made in this statement.

in this experiment by the reaction of hydrochloric acid with lead is therefore a compound of lead.

These experiments show that the interaction of lead and boiling concentrated hydrochloric acid produces a gas (which you have not examined) and a compound of lead and hydrochloric acid, or some constituent of hydrochloric acid; and that the compound of lead is a white, crystalline solid, which dissolves slowly in boiling water, and crystallises again as the water cools.

Experiment III.—*To determine whether a salt is formed by the reaction of lead oxide and hydrochloric acid; and if a salt is formed, to compare it with the salt produced by the interaction of lead and hydrochloric acid.*

To about an eighth of a test-tubeful of powdered lead mon-oxide (litharge) in a basin add about a test-tubeful of diluted hydrochloric acid (one part concentrated acid and two parts water), and boil for some minutes, *in a draught place*; pour off¹ the liquid *while it is boiling* into a beaker; add another test-tubeful of diluted hydrochloric acid to the lead oxide that has not dissolved, and boil for some minutes; then pour off the boiling liquid into the same beaker as before. *Notice that gas is not given off as the lead oxide dissolves in the acid.* Now pour some distilled water on to the solid in the basin wherein the acid was boiled with the lead oxide; boil for some minutes, and pour the hot liquid into the same beaker as before.

When you have finished this experiment try to find out why you are directed to add the water and to boil.

Add a good deal of distilled water to the contents of the beaker (at least three times as much water as the bulk of acid liquid in the beaker), and cool by setting the beaker in cold water. Pour off the cold liquid from the white, crystalline solid that has formed; wash this solid two or three times with cold water, as directed in the last experiment, *using less than quarter a test-tubeful of water each time.* Drain off the last wash-water from above the solid as completely as you can; then add about

¹ If you take hold of the hot basin with tongs *be sure that the tongs do not touch the liquid in the basin*; for if they do, some of the material of which the tongs are made will dissolve in the acid.

two or three test-tubesful of distilled water to the washed solid, and boil until the solid dissolves. Allow to become cold, and then pour off the water from the solid that crystallises out on cooling. Now test this white, crystalline solid for a chloride, and for lead, as directed in the last experiment (p. 75).

The results of this experiment show that a white, crystalline solid is produced by the interaction of boiling hydrochloric acid and lead monoxide; that this solid dissolves slowly in boiling water and crystallises as the liquid cools; and that this solid is a compound of lead and hydrochloric acid, or some constituent of hydrochloric acid.

Putting together the results of Experiments II. and III., it is extremely probable that the salt formed by the interaction of hot concentrated hydrochloric acid and lead is the same as the salt formed by the interaction of hot somewhat diluted hydrochloric acid and lead monoxide.

The results of the experiments performed in the present lesson, taken with the results of Experiment I. of Lesson XV., make it very probable that the same salt is produced whether copper or copper oxide reacts with nitric acid, and that the substitution of lead monoxide for lead, in the reaction with hydrochloric acid, does not alter the composition of the salt which is obtained. *The only way of testing this probability would be to make accurate quantitative analyses of the products of the various reactions.*

These experiments evidently point to two methods for the preparation of salts, namely, by the reaction of a metal with an acid, and by the reaction of an oxide of a metal with an acid.

These results suggest for inquiry such questions as the following. Is the same salt always obtained by the reaction of an acid with a metal as is formed by the reaction of that acid with an oxide of the same metal? Does a definite acid always produce the same salt by its interaction with a specified metal? Or may several salts be obtained by the reaction of the same acid with the same metal? If a metal forms more than one oxide, does each oxide react with any specified acid to form its own salt? Some of these questions will be examined in the following lessons.

LESSON XVII

EXAMINATION OF THE INTERACTIONS OF METALLIC OXIDES
AND ACIDS—*continued*

Apparatus and materials required.—Flask about 8 oz. and one about 2 oz. capacity. Good caoutchouc cork with two holes to fit larger flask. Wide-mouthed bottle, about 2 oz., with caoutchouc cork with two holes to fit the bottle. Hard glass tubing about 6 inches long and $\frac{1}{2}$ to $\frac{3}{4}$ inch diameter, with corks to fit it. Ordinary glass tubing. Files. Thin earthenware crucible. Funnel tube. Lead monoxide, lead dioxide, and red lead. Granulated zinc. Litmus. Common salt in lumps. Solution of silver nitrate. Lime water. Alcohol. Solution of oxalic acid. Tapers. Glass wool or asbestos wool.

Your experiments have shown that probably the same zinc sulphate is produced by the interaction of zinc oxide and sulphuric acid as by the interaction of zinc and sulphuric acid (*Experiment I., Lesson XII.; and Experiment I., Lesson XIV.*); that probably the same copper nitrate is formed whether copper, or copper oxide reacts with nitric acid (*Experiment I., Lesson XV.; and Experiment I., Lesson XVI.*); and that probably the same lead chloride is obtained whether hydrochloric acid reacts with lead or with lead monoxide (*Experiments II. and III., Lesson XVI.*).

Now the reaction of zinc and diluted sulphuric acid produced hydrogen, besides the salt zinc sulphate (*Experiment II., Lesson IX.*); and the reaction of tin with concentrated hydrochloric acid produced hydrogen, besides the salt tin chloride (*Experiment II., Lesson XIV.*). Note also that hydrogen was obtained by the interaction of diluted sulphuric acid and either magnesium or iron (*Experiment II., Lesson IX.*); and that the

reaction of copper and nitric acid produced a gas besides forming copper nitrate (*Experiment I., Lesson XV.*) But neither hydrogen nor another gas was produced in the reaction between any of the acids and any of the metallic oxides which you have examined.

Surely something besides the salt must be produced when an acid reacts with a metallic oxide? What is this something likely to be? Metals are elements; therefore the hydrogen that was produced in the reactions between various metals and sulphuric or hydrochloric acid must have come from the acids, or perhaps from the water with which the acids were diluted (for concentrated hydrochloric acid contains some water). Assume that the hydrogen came from the acid used. *Experiments I. and II. of Lesson X.* showed that water is formed by the union of hydrogen and oxygen. Hence, perhaps water is produced, besides a salt, when a metallic oxide reacts with an acid. You must put this hypothesis to the test of experiment.

Experiment I.—*To determine whether water is formed when dry hydrochloric acid gas reacts with lead monoxide.*

- Hydrochloric acid is chosen because that acid can be obtained as a gas which can be dried.

Heat about a test-tubeful of powdered lead monoxide (litharge) in a thin earthenware crucible, over a low flame, till it is quite dry.

While the lead monoxide is being dried set up an apparatus as shown in figure 27.

The apparatus consists of a flask of about 250 c.c. (say 8 oz.) capacity, fitted with a caoutchouc cork carrying a funnel tube and a piece of glass tubing which passes downwards through a good cork in a small wide-mouthed bottle (A) of about 60 c.c. (2 oz.)

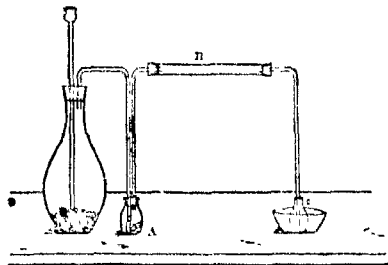


FIG. 27.

capacity; this bottle is connected with a piece of hard glass tubing (B) about 150 mm. long and 12 to 18 mm. diameter (say,

6 inches by $\frac{1}{2}$ to $\frac{3}{4}$ inch), and this tube carries a piece of ordinary glass tubing about 220 mm. (9 inches) long, which is bent downwards and dips into a small, clean flask (C); the small flask is placed in a basin containing cold water. The apparatus must be arranged so that the tube of hard glass can be heated. *The whole apparatus should be placed in a draught place.*

Fill the bottle A to about one-half with conc. sulphuric acid, taking care that the acid does not touch the neck of the bottle as you pour it in; place a good many lumps of common salt in the large flask; transfer enough of the dried lead monoxide, while it is still warm, to the tube of hard glass to fill this tube to about three-fourths when the lead oxide is packed very loosely into the tube; and insert a loose plug of asbestos, or glass wool, that has been thoroughly dried by heating, into each end of the tube.

Now put the apparatus together as represented in figure 27. Pour a little conc. sulphuric acid down the funnel tube on to the common salt in the large flask. A reaction soon begins and hydrochloric acid gas is given off; this gas is dried by bubbling through the conc. sulphuric acid in the bottle (conc. sulphuric acid readily absorbs and combines with water), and the dried acid gas then comes in contact with the dried lead monoxide in the tube of hard glass. After a few minutes heat the tube B gently, waving the flame from end to end of the tube, and gradually raising the temperature.

If the evolution of hydrochloric acid gas slackens pour a little more conc. sulphuric acid down the funnel tube: towards the end of the process it may be necessary to warm the flask which contains the common salt and sulphuric acid; this may be done by slipping a water-bath containing hot water under the flask.

Continue to heat the tube B—a high temperature is not required—until a fair quantity of liquid (say a tenth of a test-tubeful) has collected in the little flask that is surrounded by cold water; then disconnect the apparatus, and remove the tube of hard glass and the small flask containing the liquid.

Now compare the liquid in the flask with an aqueous solution of hydrochloric acid. Notice that white clouds are produced when a rod is dipped in solution of ammonia and is then held

near the surface of either liquid; notice also that both liquids dissolve zinc with evolution of hydrogen; that both turn blue litmus red; and that both give white curdy precipitates, that darken in sunlight, with silver nitrate solution.

The liquid that has been formed is evidently water containing hydrochloric acid gas dissolved in it; the excess of hydrochloric acid gas, over and above what has been used in the reaction with lead monoxide, has passed out of the tube B, and some of that excess has dissolved in the water produced in the reaction.

The results of this experiment show that water has been formed by the interaction of dry hydrochloric acid and heated lead monoxide.

In *Experiment III. of last Lesson* you obtained chloride of lead by the reaction of lead monoxide with a solution of hydrochloric acid gas: hence, it is probable that lead chloride has been formed in the present experiment. Now you know that lead chloride dissolves slowly in boiling water, and you know a reaction which is characteristic of compounds of lead in solution, and also a reaction that characterises chlorides in solution (see pp. 75 and 67). On that knowledge, supplemented by the fact that lead monoxide does not dissolve in water, devise a method for finding out whether there is any lead chloride mixed with the unchanged lead monoxide in the tube B; then apply the method you devise, and note the results.

The results of this experiment show that when dry hydrochloric acid gas reacts with dry lead monoxide, water and lead chloride are produced.

As you have found a marked similarity between the reactions of various metallic oxides with solutions of different acids (oxides of lead, zinc, and copper; and the acids sulphuric, hydrochloric, and nitric, have been used in your experiments), you seem justified in concluding that, as water is a product of the interaction of hydrochloric acid and lead oxide, water will probably be formed in the interactions between other acids and other metallic oxides.

This provisional conclusion has been shown to be correct by

the careful, quantitative, study of the interactions of acids and metallic oxides.

The results of some of the experiments made in *Lessons XIV., XV., and XVI.* show that, in many cases, the products of the reaction between a metal and an aqueous solution of an acid are a salt and hydrogen; but that in one case, at least (copper and nitric acid), the gas given off in quantity is not hydrogen. These results also make it probable that the products of the reaction between a metallic oxide and an acid are a salt and water.

At the end of *last Lesson* certain questions suggested themselves for experimental investigation (see p. 77). Answers must now be found to some of these questions. At present we shall take these questions: If a metal forms more than one oxide, does each oxide react with a determinate acid to produce, what may be called, its own salt? Are water and a salt the only products of the interaction of an acid and a metallic oxide? To find answers to these questions it is necessary to extend our examination of the reactions which occur between acids and metallic oxides.

Experiment II.—*Lead forms three oxides: litharge, red lead, and the puce-coloured oxide. Litharge reacts with hydrochloric acid to produce lead chloride and water; are the products of the reaction of this acid with the other oxides of lead the same as the products of the reaction of the acid with litharge?*

A. *To examine the reaction between red lead and hydrochloric acid.*

On to a little red lead in a test-tube pour enough diluted hydrochloric acid (about one part concentrated acid to two parts water) to fill the tube to about one-half, and warm the tube over a small flame. A visible reaction soon begins, and a gas with an exceedingly disagreeable and irritating smell is given off; if you hold the tube against white paper and look down it, you will see that the gas has a yellowish colour. Boil for a minute or two; the colour of the solid in the tube changes

from red to a dull reddish brown; and as the boiling is continued the solid becomes somewhat lighter in colour. Let the solid settle, and at once pour off the hot liquid into a beaker (if any visible change occurs in this liquid as you pour it into the beaker note what you see); pour a little distilled water on to the solid in the test-tube, shake up, let settle, and pour the water away. Now half fill the tube containing the solid with distilled water, boil for a few minutes, and pour the hot liquid into the beaker which contains the acid liquid poured off after the first treatment with boiling hydrochloric acid. Boil the solid that remains in the test-tube with a fresh quantity of distilled water, and pour away the hot liquid; once more repeat the treatment with boiling water, and pour away the hot liquid. Now add about a fourth of a test-tubeful of hydrochloric acid of the same dilution as was used before to the solid in the test-tube; boil for a minute or two—notice that the badly smelling, yellowish, gas is given off again—allow to settle, pour off the hot liquid, boil the residue with water, and pour away the hot water when the solid matter has settled. A small quantity of a brownish coloured solid, mixed perhaps with some lighter specks, remains in the tube. Boil this solid for some time with hydrochloric acid of the same dilution as was used before; if any dark coloured solid remains, wash it with a little cold water, and then boil it with water two or three times. Again boil the solid that is left with hydrochloric acid, and repeat the treatment with water. The whole of the reddish brown solid at last disappears. Notice that the badly smelling, yellowish coloured, gas is given off each time you boil the dark coloured solid with hydrochloric acid.

Turn to the beaker containing the liquids poured off from the tube wherein the boilings with acid and water were conducted. A white crystalline solid has settled down in the beaker. Pour off the liquid; wash the solid two or three times, by shaking with *very small* quantities of *cold* water and pouring off the liquid; then add about three test-tubeful of water, and boil for some minutes. The solid dissolves in the boiling water; it behaves as the lead chloride did which you prepared from litharge in *Experiment III., Lesson XVII.* Prove that this solution in hot water gives the reaction with alcohol and dilute sulphuric acid

characteristic of lead compounds in solution, and also the reaction with a drop of diluted nitric acid and silver nitrate solution characteristic of chlorides in solution (see pp. 75 and 87). The white crystalline solid is lead chloride; and, as far as you can judge from your experiments, it is the same lead chloride as that prepared from litharge; quantitative experiments have confirmed this conclusion.

Red lead has reacted with hot hydrochloric acid to produce the same salt, namely lead chloride, as is produced by the reaction of hot hydrochloric acid with lead monoxide (litharge). But this salt is not the only product of the reaction between red lead and hot hydrochloric acid: a badly smelling, yellowish, gas was given off which was not obtained when lead monoxide was used; and a reddish brown solid, differing in appearance from either red lead or litharge, remained in the tube, but this solid was changed, by repeated boiling with hydrochloric acid, into lead chloride and the badly smelling, yellowish, gas.

It is advisable to boil a little litharge with hydrochloric acid (one part conc. acid to two parts water), and to convince yourself that the badly smelling gas obtained when you used red lead is not given off in this reaction.

The results of this experiment show that the reaction between hot diluted hydrochloric acid and red lead resembles, but is not the same as, the reaction between that acid and litharge. Lead chloride is produced in both reactions [water is also formed in both reactions]; but when red lead is used there are (at least) two other products of the reaction, namely, an extremely badly smelling, yellowish, gas, and a reddish brown solid which is slowly converted by boiling hydrochloric acid into lead chloride and the badly smelling, yellow, gas.

B. *To examine the reaction between the puce-coloured oxide of lead and hydrochloric acid. Repeat part A of this experiment, but use the puce-coloured oxide of lead (lead dioxide, also called lead peroxide) instead of red lead. Notice that a gas is given off with the same irritating odour, and the same colour, as the gas which was produced in the reaction with hydrochloric acid and red lead. [Exact experiments have shown that the same gas is*

given off whether red lead or lead dioxide is used.] Notice also that the whole of the lead dioxide changes fairly rapidly to a nearly white solid; and that this solid dissolves completely in boiling water after it has been washed a few times with cold water. By performing the necessary tests prove that this white solid is lead chloride.

The results of this experiment show that the reaction between hot diluted hydrochloric acid and lead dioxide resembles, but is not the same as, the reaction between that acid and red lead. Lead chloride and a yellow, badly smelling, gas are produced in both reactions [water is also formed in both reactions]; but when red lead is used there is (at least) one other product of the reaction, namely, a reddish brown solid, which is, however, finally changed into lead chloride and the yellowish gas that smells so badly.

Experiment III.—*To compare the reddish brown solid produced in the earlier stage of the reaction of hydrochloric acid and red lead with lead dioxide.*

It seems not unlikely, from the results of *Experiment II.*, that the reddish brown solid produced in the first part of the reaction of hot hydrochloric acid with red lead may be lead dioxide; for the appearances of the two substances were alike, and both were changed, eventually, into lead chloride and the yellow, smelling, gas by reacting with hydrochloric acid. Accurate quantitative experiments, which you cannot perform at this stage, would be required to prove the identity of the two solids; but you can examine qualitatively the reactions of these solids with some reagent, and obtain results which will either increase, or diminish, the probability that the solids are the same substance.

Prepare some of the brownish solid from red lead, by shaking, and slightly warming, red lead for a few minutes with diluted hydrochloric acid (one part conc. acid to two parts water), washing what remains with cold water, boiling two or three times with water, and pouring off the water as completely as possible.

Mix this brownish solid in a test-tube with about one-sixth of a test-tubeful of diluted sulphuric acid, add the same volume of a solution in water of oxalic acid, and warm. A reaction

evidently occurs, and a colourless gas comes off; place a little lime water in a clean test-tube, and hold this tube so that any gas coming from the other tube may fall into the lime water. (See figure 26, p. 70.) On shaking the tube containing the lime water, after a few moments, the formation of a white precipitate, shows that the gas produced by the reaction of diluted sulphuric and oxalic acid solutions on the brownish solid is carbon dioxide.

Repeat this reaction with diluted sulphuric acid and a solution of oxalic acid, but use a little lead dioxide in place of the brownish solid obtained from red lead; in this case also carbon dioxide is given off.

Repeat the reaction, using lead monoxide in place of the dioxide; no gas is given off.

The results of this experiment show that the brownish solid produced in the earlier stages of the reaction between red lead and diluted hydrochloric acid may very possibly be lead dioxide.

Putting together the results of the experiments of this lesson, you are justified in concluding that although a chloride of lead, and very probably the same chloride of lead, is produced by the interaction of hot hydrochloric acid and either lead monoxide, lead dioxide, or red lead, nevertheless the reactions between that acid and the three oxides of lead show distinct differences. With lead monoxide no gas is given off; but a very badly smelling, yellowish, gas is evolved in the reaction of the acid both with red lead and with lead dioxide. When red lead is used the earlier stages of the change are marked by the production of a brownish solid (which eventually reacts with the acid) which may very possibly be lead dioxide.

We shall not turn aside to pursue the inquiries suggested by the results of the experiments of this lesson; for instance—What is the yellow badly smelling gas? Do the different oxides of the same metal always produce, finally, the same salt by their reactions with the same acid? The experiments made in the present lesson have sufficed to answer one of the questions which arose from the results of former experiments on the re-

actions between acids and metallic oxides (see p. 82); you know now that water and a salt are not always the only products of the interaction of an acid and a metallic oxide. And the results of the experiments made in this lesson will prepare you for the statement, which will be illustrated indirectly in *Lesson XIX.*, that different salts are sometimes formed by the interaction of one and the same acid with different oxides of the same metal.

LESSON XVIII

EXERCISES ON THE CLASSIFICATION OF OXIDES AS BASIC AND ACIDIC OXIDES, AND PEROXIDES

Apparatus and materials required.—Red and blue litmus solutions, and papers. Starch. Potassium iodide solution. Sodium carbonate. Granulated zinc. Platinum wire. Piece of blue glass. Silver nitrate solution. Splints of wood.

In *Lessons XI. and XII.* you learnt to distinguish *basic oxides* from *acidic oxides*; and in other lessons you have learnt something of the reactions of those elements (metals) which form basic oxides.¹ In the last lesson you had to deal with two oxides, red lead and lead dioxide, which reacted with hydrochloric acid to form (very probably) the same salt as that produced by the reaction of the same acid with lead monoxide, but which two oxides also produced a gas (by reacting with hydrochloric acid) which was not formed when lead monoxide was used. These two basic oxides, red lead and lead dioxide, differed, therefore, from the basic oxides (zinc oxide, copper oxide, lead monoxide, and potassium oxide) you had examined in previous lessons.

It is convenient to include in one class those metallic oxides which react with hydrochloric acid to produce salts (chlorides), and also that yellowish coloured, badly smelling, gas the formation of which you noticed in the cases of red lead and lead dioxide. This gas is called *chlorine*. Oxides of this class also react with hot concentrated sulphuric acid to give off oxygen [forming likewise salts—sulphates—and water]. Oxides of this class are generally called *metallic peroxides*.

Some metallic peroxides react with water to form acids, and

¹ Notice that this statement does not assert that all the oxides of all metals are basic.

with potash to form salts; they are, therefore, acidic. But they also react with hydrochloric acid to form chlorides and chlorine, and with conc. sulphuric acid to form sulphates and oxygen. It is convenient to distinguish such metallic peroxides as *acidic peroxides*.

You have now some acquaintance with oxides belonging to four classes: *acidic oxides*, which react with basic oxides to form salts, and many of which dissolve in water to form acids; *basic oxides*, which react with acids to form salts and water, only; *basic peroxides*, which react with hydrochloric acid to form chlorides and also chlorine [and water], and with hot concentrated sulphuric acid to form sulphates and also oxygen [and water], and which do not form acids by reacting with water, nor salts by reacting with potash; and *acidic peroxides*, which react with hydrochloric acid and sulphuric acid similarly to basic peroxides, but also form acids with water, and form salts by reacting with potash.

The object of the present lesson is to illustrate the classification of oxides into the four classes of acidic oxides, basic oxides, acidic peroxides, and basic peroxides. Notice that this statement does not assert that all oxides belong to one or other of these classes.

You are given four oxides, and you are asked to determine to which of the four classes named above - basic oxides, acidic oxides, acidic peroxides, and basic peroxides - each oxide belongs.

For use in the experiments you are given sulphuric and hydrochloric acids, and potash solution (a solution of basic potassium oxide).

Refer back to *Lesson XIII.*, where the determination of the basic or acidic character of several oxides was worked out in detail.

Examine the oxides separately. Begin by finding whether the oxide dissolves in water; if it does, try the effect of red and blue litmus on different portions of the solution; if it does not appear to dissolve in water, shake with water and try the litmus reactions.

Note.—If an oxide dissolves in water to form a coloured solution it is advisable to use litmus paper rather than litmus solution; let a drop of the coloured solution fall on to blue litmus paper, and another drop on to red litmus paper, and then wash the papers with distilled water.

If the results of the litmus reactions point to an oxide being acidic, neutralise some potash solution by a solution of the oxide, and evaporate, *but not to dryness* (it may be necessary to dissolve the oxide in a hot solution of potash; compare directions on p. 57); collect, and *dry thoroughly*, the solid that separates when the liquid is cold; dissolve the dried solid in water, and examine the reactions of that solution towards litmus, sodium carbonate, and zinc; also test the dried solid for potassium by the flame reaction (see p. 54). You will thus make certain whether the oxide is or is not *acidic*. Then boil a little of the oxide with hydrochloric acid (about equal parts conc. acid and water), and notice whether chlorine is, or is not, given off;¹ then heat a small quantity of the oxide with about quarter a test-tubeful of concentrated sulphuric acid (*see paragraph in italics* on p. 91), and determine whether oxygen is given off or not. You will thus determine whether the acidic oxide is also a peroxide, that is, whether the oxide under examination belongs to the class of *acidic peroxides*.

If the results of the litmus reactions point to the oxide being basic, or if no change is brought about in the colour of either red or blue litmus, try the effect of boiling a little of the oxide with fairly concentrated hydrochloric acid (about equal parts of conc. acid and water); noting any change of colour, whether chlorine is or is not given off,¹ and whether the oxide dissolves easily or not. If the oxide dissolves in the hydrochloric acid, even slightly (whether chlorine is given off or not), boil more

¹ If a piece of filter paper is dipped into a little freshly-made, very thin starch paste, and then into a dilute solution in water of potassium iodide, such paper will turn blue (or brownish blue) when it comes into contact with chlorine (you will understand the reaction that occurs at a later stage). This is not a reaction that is characteristic of chlorine, as some other substances produce the same effect; but it may be used in the present experiments to aid the senses of smell and sight. In applying this test take care that none of the hydrochloric acid is allowed to spurt on to the paper

hydrochloric acid in the draught place with the oxide, adding the oxide in small successive portions, till the acid ceases to dissolve the oxide; filter, and evaporate the filtrate, *but not quite to dryness*; collect, and *thoroughly dry*, the solid that separates; dissolve the solid in water, and examine the reactions of the solution towards litmus, sodium carbonate, and zinc; also test the solution for a chloride* (p. 67). You will thus find out whether the oxide is *basic*; and, from the reaction with hydrochloric acid, you will have obtained an indication whether it is also a peroxide.

Note.—If no solid that can be collected and dried is obtained by dissolving in hydrochloric acid and evaporating, try dissolving some of the oxide in diluted sulphuric acid and evaporating as directed above.

If the results of the reaction with hydrochloric acid have indicated a basic peroxide, heat another small portion of the oxide with about quarter a test-tubeful of concentrated sulphuric acid, and find out whether oxygen is given off. The result will determine whether or not the oxide belongs to the class of *basic peroxides*.

Take great care in heating with concentrated sulphuric acid; see that the solid is well mixed with the acid; hold the tube in a test-tube holder; heat very gently at first; do not let the flame play on the tube above where the acid is; keep the mouth of the tube pointed away from you; do not let your hand be under the tube at any time.

The results of your examinations of the four oxides should be drawn up in such a form that they may be easily compared. The following tabular arrangement answers well: the results of three actual series of experiments are given.

	I.		II.				III.	IV.
	<i>Shaken with water, litmus added</i>		<i>Neutralized by potash, &c., solid obtained dissolved in water and examined by</i>				<i>Heated with hydrochloric acid</i>	<i>Heated with concentrated sulphuric acid</i>
		<i>Sodium carbonate.</i>	<i>Zinc.</i>	<i>Litmus</i>	<i>Flame test</i>			
OXIDE M.	Blue to red.	No effect.	No effect	No effect	Flame coloured lavender-violet.		No chlorine given off.	No oxygen given off

OXIDE M is an *acidic oxide*; because it combines with a basic oxide, namely potassium oxide, to form a salt. It is not a peroxide, because it does not give off chlorine by reacting with hydrochloric acid, nor oxygen by reacting with concentrated sulphuric acid.

	I.	II.	III.				IV.
	<i>Shaken with water; litmus added.</i>	<i>Boiled with hydrochloric acid.</i>	<i>Solution in hydrochloric acid evaporated, &c., solid obtained dissolved in water and examined by</i>				<i>Heated with concentrated sulphuric acid.</i>
			<i>Sodium carbonate.</i>	<i>Zinc.</i>	<i>Litmus.</i>	<i>Chloride test</i>	
OXIDE P.	No effect.	Dissolved easily; chlorine given off.	No effect.	No effect.	Blue slightly reddened.	Positive result.	A little oxygen came off.

OXIDE P is a *basic peroxide*; because it reacts with hydrochloric acid to form a salt, and at the same time chlorine is given off, and it also reacts with concentrated sulphuric acid to give off oxygen.

	I.	II.				III.	IV.
	<i>Shaken with water, litmus added.</i>	<i>Neutralised by potash, &c., solid obtained dissolved in water and examined by</i>				<i>Boiled with hydrochloric acid.</i>	<i>Heated with concentrated sulphuric acid.</i>
		<i>Sodium carbonate.</i>	<i>Zinc.</i>	<i>Litmus.</i>	<i>Flame test.</i>		
OXIDE S.	Blue to red.	No effect.	No effect.	No effect.	Flame coloured lavender-violet.	Chlorine given off.	Oxygen given off.

OXIDE S is an *acidic peroxide*; because it combines with a basic oxide, namely potassium oxide, to form a salt; and it also gives off chlorine by reacting with hydrochloric acid; moreover, it gives off oxygen when it reacts with concentrated sulphuric acid.

LESSON XIX

FURTHER EXAMINATION OF THE INTERACTIONS BETWEEN ACIDS AND METALS

Apparatus and materials required.—Iron filings. Platinum wire. Emery paper. Calico.

The results obtained in *Experiment II., Lesson XVII.*, showed that the reactions of an acid with different oxides of the same metal are not always identical. Each of the three oxides of lead examined in that experiment reacted with hydrochloric acid to produce what was very probably the same salt (lead chloride), but some of the other products of the reactions were different. [Exact quantitative experiments have shown that the same chloride of lead is produced whether hydrochloric acid reacts with lead monoxide, red lead, or lead dioxide.]

You know from the experiments in former lessons that the same salt is often produced by the reaction of an acid with a metal as is formed when the oxide of that metal reacts with the acid: for instance, lead chloride by the reaction of hydrochloric acid with lead or lead monoxide; copper nitrate by the reaction of nitric acid with copper or copper oxide; and zinc sulphate by the reaction of sulphuric acid with zinc or zinc oxide. We wish at present to find out whether an interaction between an acid and a metal ever results in the production of more than one salt.

Experiment I.—*Preparation of the sulphate of iron called ferrous sulphate by the interaction of iron and sulphuric acid.*

Pour about two test-tubesful of diluted sulphuric acid (one part conc. acid to ten parts water) into a basin; heat the liquid, and add about one-fifth of a test-tubesful of iron filings; warm

for a few minutes until gas comes off freely, and until about half of the liquid is removed by evaporation, then remove the lamp, and pour the liquid in the basin through a filter, and collect the filtrate in another basin.

What is the gas that is given off in this reaction?

A pale greenish, crystalline, solid is deposited as the liquid cools. When the liquid is cold pour off the solution from above the crystals, dry the solid *thoroughly* by pressure in calico, dissolve a *little* of the dried solid in cold water (*keep the rest of the solid*), and prove the presence of a sulphate by adding barium nitrate solution and getting a white precipitate which does not dissolve in diluted hydrochloric acid.

Prove the presence of iron in the dried solid: for this purpose make a small loop on the end of a piece of *clean* platinum wire (the wire is cleaned by rubbing with emery paper, then dipping it into conc. hydrochloric acid in a test-tube, and heating in a Bunsen flame; these processes are repeated until the wire does not impart the slightest colour to a hot, non-luminous, flame); wet the loop, and dip it into powdered borax; then heat in a Bunsen flame until the borax melts to a clear glass-like mass which fills the loop; now take an *extremely small* piece of the dry powdered solid on to the borax, and heat in the non-luminous flame until all is thoroughly melted. On looking at the borax while it is hot you see that it is coloured reddish green, and if you observe carefully you will notice that the colour becomes greener as the borax cools. Now lower the flame, and turn off some of the air that enters the Bunsen lamp until the tip of the small flame is just luminous; then heat the borax in this luminous tip for at least three minutes, and observe the colour of the transparent borax; it is distinctly greener than it was after heating in the non-luminous flame.

Clean the platinum wire, by crushing the borax, then rubbing with emery paper, dipping the wire into conc. hydrochloric acid, and heating in the Bunsen flame. Make a fresh *borax bead* (the little piece of melted borax held in the loop of the platinum wire is called a borax bead); take on to it an *extremely small* fragment of iron, and repeat the tests that you have performed with

the dried solid obtained by dissolving iron in diluted sulphuric acid. The results are the same as before.

Iron, and compounds of iron, dissolve in melted borax, and impart a reddish green colour to the borax when heated in a hot, non-luminous, flame; but when the heating is carried out in a luminous flame the borax is coloured very pale green with a tinge of yellow. These reactions are characteristic of iron and compounds of iron. (You will learn about the reactions which occur at a later part of the course.)

This experiment shows that the pale green crystalline solid obtained by dissolving iron in warm diluted sulphuric acid, under such conditions that undissolved iron is present while the process of solution is proceeding, is a sulphate of iron.

Experiment II.—*Preparation of another sulphate of iron, called ferric sulphate, from the sulphate made in Experiment I.*

Now turn back to the remainder of the pale green sulphate of iron you have made. Dissolve this in about a test-tubeful of diluted sulphuric acid in a basin, evaporate almost to dryness over a very low flame, stirring constantly; let cool, add another test-tubeful of diluted sulphuric acid, and again evaporate to dryness over a very low flame, with constant stirring. The pale green, crystalline, solid has changed to a yellowish white, non-crystalline mass; place the basin on a sand tray in the draught place, and continue to heat over a low flame, until the solid is quite dry, stirring constantly as the drying proceeds. Repeat the borax-bead test for iron with an extremely small piece of this dried solid; the results show that the substance is a compound of iron. Dissolve a little of the dried solid in dilute hydrochloric acid and add barium nitrate solution; the formation of a white precipitate shows that the substance is a sulphate.

This experiment shows that a second sulphate of iron is obtained by evaporating a solution of the green, crystalline, sulphate in diluted sulphuric acid, under such conditions that the evaporating liquid is in contact with air and is not in contact with undissolved iron.

A consideration of the conditions under which the buff-coloured sulphate of iron was produced from the green, crystalline, sulphate shows that the change occurred in presence of plenty of hot sulphuric acid, and that the hot liquid was surrounded by air. Hence it is possible that the buff-coloured sulphate may contain more sulphuric acid, or more of some constituent of sulphuric acid, and perhaps also more oxygen, relatively to the same weight of iron, than the green, crystalline, sulphate. You cannot, at present, put this guess to a direct experimental test; but you may throw some light on the question of the compositions of the two sulphates of iron by experiments which bear on that question.

Experiment III.—*Change of the buff-coloured sulphate of iron made in Experiment II. into the green sulphate of iron made in Experiment I.*

Place most, *but not quite all*, of what remains of the buff-coloured sulphate of iron in a small basin, add about a test-tubeful of diluted sulphuric acid, and warm till the solid dissolves; then shake in about one-fifth (or rather less) of a test-tubeful of iron filings, and warm for some minutes; now pour the liquid through a filter, and let the filtrate cool. A pale green solid, which is evidently the crystalline sulphate of iron, separates as the liquid cools.

You seem to have transformed the buff-coloured sulphate into the green sulphate by adding iron to the former. Comparing this result with that obtained in the second experiment, where the green sulphate was changed to the buff-coloured sulphate by adding sulphuric acid (and perhaps oxygen), you may conclude, provisionally, that the two sulphates of iron differ in the relative quantities of iron and sulphuric acid, or constituent of sulphuric acid, they contain. This conclusion has been verified by accurate quantitative analyses of the two sulphates.

Experiment IV.—*Reactions of potash with solutions of the two sulphates of iron.*

Dissolve a little of the green sulphate of iron you made in *Experiment III.* of this lesson in cold water; add a solution of

potash, and notice the colour of the precipitate that is produced.

Dissolve what remains of the buff-coloured sulphate of iron in warm diluted sulphuric or hydrochloric acid; add a solution of potash, and notice the colour of the precipitate that is produced.

Each of these precipitates is a different hydrated oxide of iron (the precipitate from the green sulphate begins to combine with oxygen from the air the moment it is produced). Each sulphate of iron corresponds with an oxide of iron.

LESSON XX

PREPARATIONS OF SALTS

Apparatus and materials required.—Granulated lead. Pure black oxide of copper in powder. Calico.

You have now become acquainted with three methods for preparing salts: the combination of an acidic with a basic oxide, illustrated by the formations of potassium sulphate in *Lesson XI.*, and zinc sulphate in *Lesson XII.*; the interaction of a metal and an acid, illustrated by the formations of zinc sulphate and tin chloride in *Lesson XIV.*, copper nitrate in *Lesson XV.*, and the two sulphates of iron in *Lesson XIX.*; and the interaction of a metallic oxide and an acid, illustrated by the formations of copper nitrate and lead chloride in *Lesson XVI.*

Before examining another method which is used very frequently for preparing salts, it is advisable that a couple of preparations of salts by two of the methods that have been illustrated already should be worked through carefully, that a good yield of each salt should be obtained, and that the salts should be freed from other products of the reactions whereby they are prepared.

The preparations you will be asked to make are (1) the preparation of lead nitrate by the interaction of lead and nitric acid, and (2) the preparation of copper chloride by the interaction of copper oxide and hydrochloric acid.

Experiment I.—*Preparation of lead nitrate by the interaction of lead and nitric acid.*

Lead nitrate is a white crystalline solid.

Lead nitrate is only slightly soluble in conc. nitric acid, but it dissolves easily in very dilute nitric acid; on the other hand, very dilute nitric

acid has little action on lead. The object of adding sometimes acid and sometimes water is to insure the presence of enough acid to dissolve all the lead, but not so much as to cause the lead nitrate to separate from the solution.

Place about 40 grams (about a test-tubeful) of granulated lead in a basin of about 300 c.c. (about 10 oz.) capacity, set the basin on wire gauze on a tripod, *in the draught place*, add about four test-tubeful of nitric acid (equal parts conc. acid and water), warm until a reaction begins and reddish gas comes off, and then remove the lamp; the reddish gas that is given off is nitrogen dioxide, compare the reaction of copper and nitric acid in *Lesson XV.* (p. 68). When the reaction slackens place a *low flame* under the basin and continue to heat, adding a little water occasionally if white solid matter forms in the liquid, and adding a little nitric acid if the reaction slackens much. Proceed thus until the whole of the lead has dissolved; then add about a test-tubeful of water, heat for a few minutes, run the liquid through a filter into a clean basin, pour a test-tubeful of boiling water through the filter, and evaporate the whole of the filtrate, over a *low flame*, until a small quantity of the liquid deposits white crystals when it is cooled in a test-tube by running cold water on to the outside of the tube. It will probably be necessary to evaporate the liquid till the total quantity of it is about 60 c.c. (say a couple of test-tubeful). Now let the liquid in the basin cool: the process may be hastened by floating the basin in cold water; pour off the liquid, into a clean basin, from the white crystalline solid that has formed—if no crystals appear when the liquid is cold evaporate a *little* further and cool—evaporate this *mother liquor* (that is, the liquid poured off from the crystals) to about half its bulk, and let it cool, when a second crop of crystals of lead nitrate will be obtained.

Pour off the mother liquor from the second crop of crystals; if the liquid amounts to more than about half a test tubeful evaporate it a *little* further, and obtain a third crop of crystals of lead nitrate.

Drain the crystals as thoroughly as possible, by tilting the basins and pressing the crystals with a glass rod; then remove the lead nitrate, by a spatula, on to a piece of dry calico, and

press between folds of calico until the solid is so dry that it leaves no wet stain when pressed in filter paper.¹

About 85 grams of lead nitrate (rather more than half a test-tubeful) should be obtained.

Keep the lead nitrate you have made; it will be used in *Lesson XXI., Experiment I.*

Experiment II.—*Preparation of hydrated copper chloride by the interaction of copper oxide and hydrochloric acid.*

Hydrated copper chloride is a green, crystalline, solid.

Place about a couple of test-tubesful of hydrochloric acid (equal parts conc. acid and water) in a basin, on wire gauze on a tripod, *in the draught place*; heat the acid nearly to boiling, and add about 20 grams *pure* black oxide of copper (about half a test-tubeful), *in small successive portions*, waiting till each portion is dissolved before you add more; if the whole of the oxide of copper does not dissolve after boiling for some minutes, add more acid, *in small quantities at a time*, until the oxide of copper just dissolves after boiling for a little time. Evaporate the greenish brown solution over a *low flame* until the formation of a film on the surface of the liquid begins, then place the basin on a sand tray, and continue to heat over a *very low flame*, *stirring constantly*, until you obtain a dry, green, crystalline, solid.

About 40 grams (say two test-tubesful) of hydrated copper chloride should be obtained.

Keep the copper chloride you have made; it will be used in *Lesson XXI., Experiment II.*

* ¹ If a filter-pump is at hand, it is advisable to collect the various preparations made in this and subsequent lessons on a circular piece of filter paper fitted over a perforated porcelain disc. The disc is placed in a funnel which passes through a cork fitted tightly into a flask which is connected with the pump.

LESSON XXI

1. PREPARATIONS OF BASIC METALLIC OXIDES

Apparatus and materials required. - Lead nitrate and copper chloride made in last Lesson. Calico. Ferrous sulphate. Flat earthenware dish about 3 inches diameter.

As you proceed with the study of the salts and the oxides of metals you will find that there is generally an oxide corresponding with the salts of a metal; that is, an oxide which can be obtained from some, or all, of these salts, and which reacts with acids to produce these salts.

The reactions observed in *Experiment IV. of Lesson XIX.*, by adding potash to solutions of the two sulphates of iron, indicated the probability of the existence of an oxide of iron corresponding with each sulphate of iron. As your acquaintance with metallic salts and oxides becomes more complete you will find that when a metal forms two, or more, salts by reacting with the same acid there is generally an oxide corresponding with each salt. You will also find that in some cases the salts corresponding with a certain oxide have not been isolated.

It is advisable, at this stage, to prepare a few metallic oxides; with the objects of becoming familiar with some of the methods of preparation of these compounds, and of realising some of the connections between the oxides and the salts of metals.

The oxides you will be asked to prepare are lead monoxide, from lead nitrate; copper oxide, from copper chloride; ferric oxide, from ferric sulphate (a solution of which will be made from the other sulphate of iron, *ferrous* sulphate); and the magnetic oxide of iron (ferroso-ferric oxide), as an example of a metallic oxide which does not form corresponding salts.

The method very often adopted for preparing a basic oxide from a salt is to dissolve the salt in water, or in a diluted acid; to add a slight excess of potash, or ammonia, solution; to wash, collect, and dry, the hydrated oxide which is thus precipitated (in some cases the precipitate is the oxide uncombined with water); and to heat this hydrated oxide, whereby water is removed and the oxide remains.

Experiment I.—*Preparation of lead monoxide from lead nitrate.*

Lead nitrate is dissolved in water, and lead hydroxide is precipitated by addition of ammonia solution; the other product of the reaction, namely, ammonium nitrate, is removed by washing with hot water wherein ammonium nitrate is soluble (lead hydroxide is insoluble in water), and the wash-water at the same time removes the excess of ammonia over and above what has been used in the reaction; the lead hydroxide is decomposed by heating to lead monoxide which remains as a solid, and water which is driven off as steam.

Lead hydroxide is a white solid, and lead monoxide is a buff yellow solid.

Dissolve about 35 grams (about half a test-tubeful) of the lead nitrate you prepared in *Experiment I., Lesson XX.*, in four or five test-tubeful of water in a basin (about 7 or 8 inches diameter), heating slightly to hasten solution; add ammonia, little by little, until after stirring thoroughly there is a smell of ammonia; boil for a few minutes, while constantly stirring the contents of the basin; allow the white precipitate of lead hydroxide to settle; add a little more ammonia; if no more precipitate is produced excess of ammonia has been added, if the ammonia produces a precipitate add more ammonia, boil again, allow the precipitate to settle, and again test if precipitation is completed by adding a little more ammonia. When precipitation is completed allow the precipitate to settle for a few minutes, and then pour off the supernatant liquid down a glass rod held against the lip of the basin; the rod serves to direct the stream of liquid and prevent it from running along the outside of the basin; pour a little water (about three or four test-tubeful) on to the solid in the basin, heat nearly to boiling, stirring thoroughly all the time, allow the solid to settle,

pour off the liquid down a glass rod, add a little more water, heat while stirring, allow the precipitate to settle, and pour off the water again; repeat this process of *washing by decantation* three or four times, and then test a little of the last washings (after filtration from suspended lead hydroxide) for a nitrate as directed on p. 70, *Experiment I., Lesson XV.* If a nitrate is not present the ammonium nitrate produced in the interaction has all been washed away; hence the solid is now pure lead hydroxide. If the washings give the reaction for a nitrate, *washing by decantation* must be continued until every trace of nitrate is removed. Now dry the lead hydroxide by pressing it between folds of calico (as described in the preparation of lead nitrate); place the solid in a flat earthenware dish, and heat over a *very low flame*, stirring frequently with a glass rod to prevent the formation of lumps, until the solid is quite dry, when the flame should be raised *very slightly* and heating continued until the solid becomes buff yellow in colour without the appearance of any red specks; now shake the solid into a dry mortar, rub it into powder with a dry pestle, and, if there are any white particles (lead hydroxide) heat again, with constant stirring, over a *very low flame*, until every particle of the solid is buff yellow in colour.

If the temperature gets too high in converting lead hydroxide into lead oxide, a little red lead may be formed by the hot lead monoxide combining with oxygen in the air.

About 15 grams of lead monoxide, sufficient to fill nearly one-fourth of an ordinary test-tube, should be obtained.

Experiment II. - *Preparation of copper oxide from copper chloride.*

Dissolve a very little hydrated copper chloride in water, and divide the solution into two parts. To one part add ammonia solution drop by drop until there is a distinct smell of ammonia after shaking thoroughly; to the other part add potash solution drop by drop until after shaking thoroughly the liquid changes the colour of a piece of red litmus paper to blue (that is, until there is an excess of potash present). You notice that ammonia produced a precipitate, but that this precipitate dissolved when an excess of ammonia was added; and that the precipitate produced by potash did not dissolve when

an excess of potash was present. It will, therefore, be necessary to use potash solution, and not ammonia solution, as a precipitant.

Hydrated copper chloride is dissolved in water, and copper hydroxide is precipitated by addition of potash solution; the other product of the reaction, namely, potassium chloride, is removed by washing with hot water wherein potassium chloride is soluble (copper hydroxide is insoluble in water), and the wash-water at the same time removes the excess of potash over and above what has been used in the reaction. The copper hydroxide is dehydrated by suspending it in water and boiling for some time; it is then collected and dried.

Lead hydroxide (see last experiment) cannot be dehydrated in this way.

Copper hydroxide is a greenish blue solid, and copper oxide is a black solid.

Dissolve in water in a basin about 10 grams (about half a test-tubeful) of the hydrated copper chloride you prepared in *Lesson XX., Experiment II.*; add potash solution gradually, with frequent shaking, until a piece of red litmus paper dipped into the liquid is turned blue; then boil until the precipitate has become black and granular; allow the precipitate to settle; decant off the liquid, pouring it down a glass rod; add a little water, and boil; then let the precipitate settle, and decant off the liquid; continue to wash by decantation with boiling water until the wash-water ceases to give the reaction with a drop of silver nitrate solution and nitric acid characteristic of a chloride (see p. 67, *Experiment II., Lesson XIV.*). When the precipitated black oxide of copper has been thoroughly washed, decant off the liquid as completely as possible, collect the solid on a filter, allow the water to drain away, remove the solid by a spatula to a flat earthenware dish, and dry it, by heating the dish, over a very low flame, stirring constantly.

About 5 grams (say one-eighth of a test-tubeful) of copper oxide should be obtained.

LESSON XXII

PREPARATIONS OF METALLIC OXIDES—*continued*

Apparatus and materials required.—Ferrous sulphate. Concentrated nitric acid. Flat earthenware dish about 3 inches diameter. Magnet. Potassium ferrieyanide. Potassium sulphocyanide. Solution of a pure ferric salt.

Experiment I.—*Preparation of ferric oxide* (red oxide of iron or iron rust) *from ferric sulphate*; the solution of ferric sulphate being prepared from crystals of ferrous sulphate (green vitriol).

Hydrated ferric oxide is a foxy-red solid, and ferric oxide is a very dark red solid.

• Dissolve about 4 grams (about one-sixth of a test-tubeful) of powdered ferrous sulphate in about two test-tubeful of diluted sulphuric acid in a basin; heat to boiling, and allow conc. nitric acid to trickle into the *boiling* solution, *one drop at a time*, until the very dark colour produced at first is removed, and the liquid becomes reddish yellow.

You will notice that the addition of a few drops of nitric acid to the boiling solution produces a very dark colour in the liquid, and that as a little more nitric acid is added to the boiling liquid there is an outrush of reddish gas from the liquid, and a decrease in the depth of colour of the solution; after a few minutes, and when about a dozen or twenty drops of nitric acid have been added, you will notice a sudden outrush of gas, accompanied by the disappearance of the dark colour from the liquid. The reactions which occur will be stated at a later part of the course; at present you may regard the nitric acid as a reagent which supplies oxygen to the ferrous sulphate, and, acting with the sulphuric acid, converts the ferrous into ferric sulphate. (Compare *Experiment II.*, Lesson XIX., pp. 95, 96.)

Cool the reddish yellow liquid, which contains ferric sulphate, then add to it a slight excess of ammonia solution; boil; let the reddish brown precipitate of hydrated ferric oxide settle; pour off the liquid from above the precipitate; wash the precipitate by boiling with water, allowing to settle, and decanting off the liquid, until a little of the wash-water ceases to smell of ammonia, and also ceases to give the reaction (see p. 55) with barium nitrate and hydrochloric acid characteristic of a sulphate (ammonium sulphate is produced in the reaction between ferric sulphate and ammonia solution); now collect the washed hydrated ferric oxide on a filter, then transfer it to an earthenware dish, and heat over a low flame, stirring frequently to expose fresh portions of the substance to the action of the heat, until a very dark red (almost black) solid is obtained.

About a gram of ferric oxide should be obtained.

Experiment II.—*Preparation of magnetic oxide of iron (ferroso-ferric oxide).*

Magnetic oxide of iron is a black solid.

When an excess of ammonia is added to a solution containing both a ferrous and a ferric salt, in such a proportion that the weight of iron in the quantity of the ferric salt present is double that of the iron in the quantity of ferrous salt present, magnetic oxide of iron is precipitated.

It is not at all easy to prepare pure magnetic oxide of iron; in the present experiment you will not obtain a pure preparation, but if the experiment is done with a fair amount of care the product will be sufficiently pure for demonstrating with it some of the characteristic properties of the oxide.

Dissolve about one-fourth of a test-tubeful of powdered ferrous sulphate in three or four test-tubesful of cold diluted sulphuric acid (if the acid is warmed some of the ferrous sulphate will be changed to ferric sulphate); measure off two portions of this solution, one portion being twice as large as the other (say two test-tubesful and one test-tubeful); convert the larger portion into a solution of ferric sulphate, as directed in *Experiment I.* (p. 105); then cool this solution thoroughly, and when it is quite cold mix it with the smaller portion of the

original solution of ferrous sulphate; to the mixed liquids add a slight excess of ammonia, boil for a few minutes, and let the black precipitate settle.

Why must the ferric sulphate solution be cold before it is mixed with the solution of ferrous sulphate?

Wash the black precipitate with boiling water, by decantation, until the wash-water ceases to give the characteristic reaction of a sulphate with barium nitrate and hydrochloric acid (see p. 55).

Why do you test for a sulphate?

Cover the washed magnetic oxide of iron with water in a beaker; place the poles of a magnet on the outside of the beaker opposite the solid, and move the magnet slowly upwards along the glass; the magnetic oxide is attracted by the magnet and is raised some little distance against the inside of the beaker. Add a little *diluted* hydrochloric acid to the washed magnetic oxide in the beaker, shake for a few minutes, *without warming*, and filter. To a portion of the filtrate add a few drops of a solution, *freshly made in cold water*, of potassium ferrieyanide (red prussiate of potash); a greenish blue colour is produced. To another portion of the filtrate add a few drops of a solution of potassium sulphocyanide; a deep red colour is produced.

Now wash a little powdered ferrous sulphate in running water for a few moments, then dissolve it in cold water, and to *separate portions* of this solution *at once* add (1) potassium ferrieyanide solution, and (2) potassium sulphocyanide solution, and notice what visible change occurs in each case. Dissolve a little *pure* ferric sulphate (or ferric chloride) in diluted hydrochloric or sulphuric acid, and to *separate portions* of this solution add (1) potassium ferrieyanide solution, and (2) potassium sulphocyanide solution, and notice what visible changes occur.

A comparison of the results of these tests with those performed with the solution in cold diluted hydrochloric acid of the magnetic oxide of iron shows you that the solution of that oxide contained both a ferrous and a ferric salt of iron (the salts must have been ferrous *chloride* and ferric *chloride*). The black oxide of iron, then, is magnetic; it dissolves in diluted cold hydrochloric acid to form both ferrous and ferric chlorides, and it is

prepared by adding ammonia to a solution containing both a ferrous and a ferric salt of iron in a certain definite proportion.

In the experiments made in this lesson, and in *Lesson XVI.*, you have prepared four metallic oxides by adding either potash or ammonia solutions, which compounds are *alkalis* (see forward, *Lesson XVII.*), to solutions of salts of the metals, and heating the hydrated oxides thus precipitated. This is the method most commonly employed for the preparation of basic oxides of metals. In former lessons you prepared several oxides by causing elements to combine directly with oxygen; magnesium oxide by burning magnesium in air, and lead oxide by heating lead in air (*Lesson V.*), iron oxide by allowing moist iron to rust in air (*Lesson IX.*), and water by burning hydrogen in air (*Lesson X.*).

. LESSON XXIII

. PREPARATIONS OF SALTS

Apparatus and materials required.—Barium nitrate. Potassium oxalate. Lead nitrate. Potassium iodide. Large basin about 8 inches diameter. Calico. Ferrous sulphate.

The methods for preparing salts which have already been illustrated are (1) the interaction of basic and acidic oxides, (2) the interaction of metals and acids, (3) the interaction of metallic oxides and acids. Of the other methods, the most commonly used are (i.) the interaction of two salts, and (ii.) the interaction of a salt and an acid. The first of these methods will be illustrated in the *present Lesson*, and the second in *Lessons XXIV*, *XXV*, and *XXVI*.

Experiment I.—*Preparation of barium oxalate (and potassium nitrate) by the interaction of solutions of barium nitrate and potassium oxalate.*

The products of the interaction of solutions of the salts barium nitrate and potassium oxalate are the salts barium oxalate and potassium nitrate. Barium oxalate is nearly insoluble in water, the other three salts are soluble in water; barium oxalate is, therefore, precipitated when solutions of potassium oxalate and barium nitrate are mixed; and the precipitate can be obtained free from the other salts by washing with water.

Barium oxalate is a white solid.

Dissolve about 10 grams powdered potassium oxalate (about one and a half test-tubesful) in about 300 c.c. (about ten test-tubesful) of water in a beaker, warming and shaking until solution is completed.

If the acid oxalate of potassium (salt of sorrel) is used, about 25 grams (about three-fourths of a test-tubesful)

should be taken; this weight will require about 700 to 800 c.c. (say 25 test-tubesful) of water for solution.

While the solution of the potassium oxalate is proceeding dissolve about 50 grams (about a test-tubesful) of barium nitrate in about 100 c.c. of water (about 13 test-tubesful), in a large basin (about 200 mm. = 8 inches diameter), warming and stirring until solution is completed.

Heat the solution of barium nitrate to boiling, and pour the solution of potassium oxalate into the boiling liquid, stirring vigorously, until no precipitate is formed when a little of the potassium oxalate solution flows into the clear liquid above the precipitated barium oxalate, that is, until precipitation is completed. Now pour off the liquid from above the white precipitate; add two or three test-tubesful of water, boil, and stir vigorously, let the solid settle, and decant off the supernatant liquid. Repeat this process of washing with hot water by decantation three times; test a little of the third lot of wash-water for a nitrate (by the reaction with conc. sulphuric acid and solution of ferrous sulphate, see p. 70), and also test a little for an oxalate (see below). If neither nitrate nor oxalate is found the washing has removed all the potassium nitrate formed in the reaction, and also all the potassium oxalate which remained over and above what was used in the chemical change. If either nitrate or oxalate is found the washing with hot water by decantation must be continued until the nitrate and oxalate are removed. When this has been done the barium oxalate is pure.

Keep the barium oxalate, without drying it, for use in Lesson XXVI.

Test for an oxalate in solution.—To the solution add a slight excess of ammonia, then acetic acid until the liquid is acid to litmus paper, and then a little calcium chloride solution; if a white precipitate forms it is calcium oxalate.

Experiment II.—*Preparation of lead iodide and potassium nitrate by the interaction of solutions of lead nitrate and potassium iodide.*

The salts lead nitrate and potassium iodide react in the proportion of almost exactly equal parts by weight; the products of the reaction are the salt lead iodide and potassium nitrate.

Lead nitrate dissolves in about four-fifths of its weight of boiling water; lead iodide is nearly insoluble in cold water, but it dissolves slightly in boiling water; potassium nitrate dissolves in about two-fifths of its weight of boiling water, but it requires about four times its weight of water at the ordinary temperature to retain it in solution; potassium iodide dissolves in about half its weight of boiling water, and in rather more than half its weight of water at the ordinary temperature.

These data show that if solutions of approximately equal parts by weight of lead nitrate and potassium iodide in boiling water are mixed, and the liquid is cooled to the ordinary temperature, the whole, or almost the whole, of the lead iodide formed will separate from the cold liquid; and if the liquid is decanted off, and evaporated until it deposits crystals on cooling, most of the potassium nitrate that has been formed will separate, with but a very little, or perhaps with none, of any excess of potassium iodide that may have remained unchanged in the reaction.

Lead iodide is a yellow, lustrous, crystalline solid; potassium nitrate separates from a solution in long, colourless crystals.

Weigh out fairly accurately 10 grams of powdered lead nitrate and 10 grams of potassium iodide; dissolve each in about a test-tubeful of boiling water; mix the two solutions in a beaker, and cool the liquid thoroughly by running cold water on to the outside of the beaker. When the liquid is quite cold pour it and the solid lead iodide on to a filter of calico placed in a funnel, and collect the filtrate in a basin; wash the lead iodide on the filter a few times with *small quantities* of cold water, and add the washings to the filtrate; evaporate the filtrate and washings to about one-fourth of its bulk, and allow it to cool.

While the liquid is cooling dry the lead iodide by squeezing the calico filter, then transferring the solid to dry calico and pressing it repeatedly.

About 12 grams of lead iodide (say, nearly one-third of a test-tubeful) should be obtained.

When the liquid which has been filtered from the lead iodide and evaporated is quite cold, decant it from the crystals that have

formed, evaporate the decanted liquid a little further, and let it cool. Now collect and dry, by pressure in filter paper, both crops of white crystals that have been produced; if these crystals are mixed with any yellow iodide of lead add just enough *cold* water to dissolve the crystals, filter from lead iodide, evaporate the filtrate nearly, *but not quite*, to dryness, cool, and collect and dry the white crystals that separate.

Prove that the white crystalline solid is a nitrate (see p. 70), and also prove that it is a compound of potassium (see p. 54).

* LESSON XXIV

INTERACTIONS OF ACIDS AND SALTS. PREPARATIONS OF
ACIDS, AND OF SALTS

Apparatus and materials required.*—Potassium chloride. Flat earthenware dish. Zinc. Sodium carbonate. Litmus solutions. Silver nitrate solution. Flask, about 10 oz., with good cork. Funnel tube. Glass tubing. Files. Calico. Platinum wire.

The products of what may be called a *normal reaction between an acid and a salt* are another acid and another salt. For instance, the salt potassium chloride reacts with sulphuric acid to produce the salt potassium sulphate and hydrochloric acid; and the salt barium oxalate reacts with sulphuric acid to produce the salt barium sulphate and oxalic acid.

In some cases secondary reactions occur between some of the interacting compounds, and other substances are produced besides the normal products of the reaction, that is to say, besides the new salt and the new acid. Sometimes the acid which is one of the products of the reaction separates, under the conditions of the reaction, into two or more bodies so completely that the acid itself cannot be isolated.

In this and the next lesson we shall examine two instances of the normal reaction between an acid and a salt; namely, the reaction of potassium chloride and sulphuric acid, and the reaction of lead nitrate and sulphuric acid. The experiments to be performed will illustrate methods that are very often employed for making acids, and also methods for making salts: for in this lesson we shall prepare hydrochloric acid solution and the salt potassium sulphate, and in the next lesson we shall make nitric acid and the salt lead sulphate.

Experiment I. *Preparation of hydrochloric acid solution and potassium sulphate, by the interaction of sulphuric acid and potassium chloride.*

As hydrochloric acid, an aqueous solution of which is to be prepared, is gaseous at ordinary temperatures, it is very easily separated from the other interacting compounds, none of which is volatile at a moderate temperature.

Potassium sulphate is a white crystalline solid, easily soluble in water or diluted acid solutions. Hydrochloric acid gas is colourless, fumes much in the air, and dissolves very easily in water.

Place about 80 grams (about a test-tubeful) of potassium chloride in a flask of about 800 c.c. (10 oz.) capacity, fitted with a

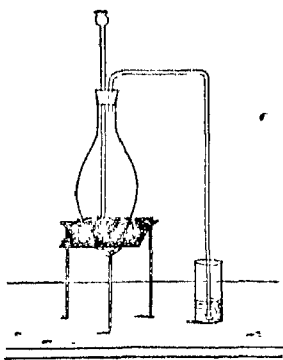


FIG. 28

good cork carrying a thistle-headed tube and a glass tube which is bent twice at right angles, the longer limb being nearly 400 mm. (15 inches) long. Set the flask on wire-gauze on a tripod, and let the glass tube dip into 6 or 8 test-tubeful of water in a beaker (see figure 28). Pour into the flask sufficient conc. sulphuric acid to completely moisten the potassium chloride, and shake until the solid and the acid are thoroughly mixed. See that the lower end of the thistle-headed tube

dips beneath the acid in the flask; and warm the flask *very gently*. A reaction begins, and hydrochloric acid gas is given off and is dissolved in the water in the beaker. Continue to heat, *over a very low flame*, shaking the flask from time to time, until the evolution of gas has nearly ceased; then, without turning out the lamp, lift the flask from the tripod, and place it in a draught place, leaving it there till it is cold. (If you put out the lamp before removing the flask, the solution of hydrochloric acid *may* run back into the hot liquid in the flask and cause a dangerous ebullition.)

Shake the aqueous solution of hydrochloric acid in the beaker

until it is thoroughly mixed, pour a very little of it into a test-tube, and add a few drops of blue litmus solution; the blue colour changes to red. Pour some more of the solution of hydrochloric acid into a test-tube, and add a few small pieces of granulated zinc; after a few minutes the zinc begins to dissolve, and a gas is given off which takes fire with a slight explosion when a taper is brought to the mouth of the tube; this gas is hydrogen. Pour about a couple of test-tubesful of the solution of hydrochloric acid into a basin, add a few drops of blue litmus solution, and then a *dilute* solution of caustic potash, drop by drop, with constant stirring, until the colour of the litmus changes to purple; the acid is now neutralised by the potash; evaporate this liquid till froth forms freely on the surface, and let it cool; collect the solid that forms on cooling, and press it between calico until it is perfectly dry; dissolve the dry solid in a little water, add a few drops of nitric acid, and then a very little solution of silver nitrate; the formation of a white, curdy precipitate, which darkens on exposure to sunshine, shows that a chloride is present. Hence the hydrochloric acid has reacted with potash to produce a salt of hydrochloric acid, that is, a chloride. To a little more of the solution of hydrochloric acid, in a test-tube, add a little solid sodium carbonate; a gas is given off. Decant this into a little lime water in a test-tube, and shake the lime water; a turbidity, due to formation of calcium carbonate, is produced in the lime water; this proves the gas to be carbon dioxide.

The solution obtained by leading into water the gas produced by the interaction of potassium chloride and sulphuric acid is therefore a solution of an acid; it dissolves a metal (zinc) giving off hydrogen, it decomposes a carbonate (sodium carbonate) giving off carbon dioxide, it turns blue litmus red, and it neutralises an alkali (caustic potash) forming a salt.

Now turn to the contents of the flask. The white solid in the flask is potassium sulphate. As some sulphuric acid, and probably also a little hydrochloric acid, will be adhering to the salt, it will be necessary to free it from these impurities. The purification can be accomplished by dissolving the potassium sulphate in water, and crystallising it; if this process is repeated

the solid salt will be obtained free from the acids, which will remain in solution in the water.

Pour three or four test-tubeful of water into the flask; warm, and shake until the solid is dissolved; pour the liquid into a basin, evaporate over a *low flame* until froth begins to form on the surface of the liquid, and allow to cool. When the liquid is quite cold, decant it from the white crystalline solid that has separated, into another basin, evaporate a little further, and let cool. Drain the first crop of crystals as thoroughly as possible; then transfer them to a piece of dry calico and press them till quite dry. Dissolve the dry crystals in a *little* warm water. Now drain, and dry, the second crop of crystals, and dissolve the dry solid in the aqueous solution of the first crop of crystals. Evaporate the liquid, over a *low flame*, until a small quantity in a test-tube deposits a white crystalline solid when it is cooled by running cold water on to the outside of the tube; then let the liquid in the basin cool; collect, and *dry thoroughly* (in calico), the crystals of potassium sulphate that have separated. The dried crystals should be tested for a potassium compound by the flame test (p. 51), and for a sulphate by the barium nitrate test (p. 55).

About 20 grams (about three-fourths of a test-tubeful of potassium sulphate should be obtained.

LESSON XXV

INTERACTIONS OF ACIDS AND SALTS - *continued*. PREPARATIONS
OF ACIDS, AND OF SALTS

Apparatus and materials required. Lead nitrate. Ferronitric sulphate. Zinc. Sodium carbonate. Litmus. Stoppered retort, about 5 oz. A flask of about 3 oz. capacity. Calico. Small earthenware dish.

Experiment I. *Preparation of nitric acid and lead sulphate, by the interaction of sulphuric acid and lead nitrate.*

Nitric acid is a liquid which is easily volatilized by heat; it can, therefore, be separated from the other interacting compounds, by causing it to volatilize and then condensing the gas to liquid by cooling. When nitric acid is heated some of it is decomposed, to water and oxides of nitrogen; the acid obtained in this experiment will not, therefore, be pure.

Lead sulphate is a white solid, insoluble in water or in diluted acid solutions. Nitric acid is a colourless, acid liquid; but the acid obtained by the method of this experiment is coloured yellowish red from the presence in it of oxides of nitrogen.

Place about 30 grams (about half a test-tubeful) of lead nitrate in a small tubulated retort of about 150 c.c. (5 oz.) capacity; if the solid is placed in a piece of glazed paper, and the edges of the paper are brought together, it is easy to shake the solid into the retort through the tubulus. Set the retort on a stand, and let its neck pass into a small flask placed in a dish of cold water (see figure 29). Pour into the retort, through a funnel, about 10 c.c. (say one-third of a test-tubeful) conc. sulphuric acid. Put the stopper into the tubulus, and warm the retort *gently*; a reaction begins after a little, and a

yellowish liquid slowly condenses in the small flask. Should the small flask get warm, cover it with some filter paper and wet this paper from time to time with cold water. Continue to heat,

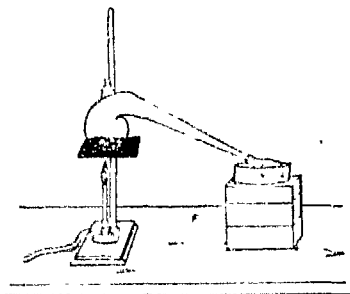


FIG. 29

over a *low flame*, until the reaction has nearly ceased; remove the retort to the draught place, taking care that the small flask containing the nitric acid does not tilt over in the water.

From 10 to 12 c.c. (about one-third of a test-tubeful) of nitric acid should be obtained.

Prove that the liquid produced in the reaction (1) reddens litmus; (2) reacts with a metal (say zinc, or copper) giving off a gas which is evidently not hydrogen as it is coloured reddish [*compare* reaction of nitric acid with copper (p. 68) and with lead (p. 99)]; (3) reacts with a carbonate (use sodium carbonate) giving off carbon dioxide; and (4) neutralises potash solution forming a solution from which on evaporation a solid separates that gives the reaction of a nitrate (see p. 70) after it has been *completely* dried: for neutralising potash use about a fourth of the quantity of acid you have prepared.

The liquid obtained by heating lead nitrate with sulphuric acid and condensing the gaseous product of the interaction is, then, an acid, and it is nitric acid.

Now turn to the contents of the retort. Quickly pour a good deal of water into the retort, *in the draught place*, shake up, and let the solid settle; pour off the liquid, and continue to wash the solid by decantation, with cold water, *until the washings are*

perfectly neutral to litmus. Only the first washings need be done in the draught place. The excess of sulphuric acid, and any nitric acid that may not have been driven off by the heating, are thus washed away, and only lead sulphate remains. *Be sure that the washing process is not commenced until the contents of the retort are quite cold*; if water is added to warm conc. sulphuric acid the acid may be projected from the vessel and may cause very serious burns. Dry the solid, after it has been thoroughly washed, by pressure between calico, and then by heating it, in a flat earthenware dish, over a very low flame.

About 20 grams (fully one-third of a test-tubeful) of lead sulphate should be obtained.

The methods employed in this and the preceding lesson for preparing nitric acid, and a solution in water of hydrochloric acid, are those generally used for making acids which can be volatilised by heat.

LESSON XXVI .

INTERACTIONS OF ACIDS AND SALTS. PREPARATIONS
OF ACIDS, AND OF SALTS—*continued*

Apparatus and materials required.—Lead oxalate. Moist barium oxalate made in *Lesson XXIII*. Apparatus to make sulphydric acid; iron sulphide; commercial hydrochloric acid diluted with twice its volume of water. Wide-mouthed bottle of about 8 oz. capacity. Calico.

Two instances of normal reactions between acids and salts will be examined in this lesson; namely, the reaction between lead oxalate and sulphydric acid giving lead sulphide and oxalic acid, and the reaction between barium oxalate and sulphuric acid giving barium sulphate and oxalic acid. These reactions illustrate the method commonly employed for preparing an acid which cannot be volatilised by heat, but which can be crystallised from water. A salt of the acid is caused to react with another acid, such a salt and such an acid being selected that the new salt formed can be separated easily from the new acid produced, and that the excess of the acid used in the reaction can be removed, or that the reaction can be accomplished without employing an excess of the acid. A lead salt of the acid wished for is very often decomposed by sulphydric acid, or a barium salt by sulphuric acid.

In examining the reactions studied in the present lesson we shall concentrate our attention on the oxalic acid, which is a product of both reactions.

Experiment I.—*Preparation of oxalic acid, and lead sulphide, by the interaction of sulphydric acid and lead oxalate.*

As oxalic acid is a solid compound which is decomposed by heating, this acid cannot be separated from the other interacting compounds

by volatilising it, as was done with hydrochloric acid and nitric acid in the last lesson. Oxalic acid can be crystallised from water; of the other compounds which take part in the reaction, lead oxalate and lead sulphide are insoluble in water, and sulphydric acid is a gas which can be readily removed from a solution by boiling.

Oxalic acid separates from an aqueous solution in white crystals; lead sulphide is a nearly black solid.

Lead oxalate is caused to react with sulphydric acid gas in presence of water; the oxalic acid that is produced dissolves in the water, and the other product of the reaction, namely, lead sulphide, remains as a solid. There is some difficulty in carrying the reaction to completion because the solid particles of lead sulphide coat the particles of lead oxalate and prevent contact between the oxalate and the sulphydric acid gas.

Place about 30 grams lead oxalate (about a test-tubeful) in a wide-mouthed bottle of about 250 c.c. (about 8 oz.) capacity, fill the bottle to about three-fourths with water, and pass in a *rapid* stream of sulphydric acid gas (made by the reaction of iron sulphide and hydrochloric acid in a fair-sized apparatus), *shaking the bottle almost constantly*, to expose fresh portions of lead oxalate to the action of the gas, until *all* the solid particles in the bottle are black, that is, until the reaction is completed. (If a beaker were used it would probably be broken during the shaking.)

From 10 to 15 minutes will be required to decompose the whole of the lead oxalate.

When the reaction is completed pour the liquid through a filter, retaining as much as possible of the black lead sulphide in the bottle; wash the solid with water three or four times by decantation, pouring the washings through the filter; place the solution that has come through the filter in a basin, evaporate it, *over a very low flame* (see Note, p. 122) to the crystallising point, and allow it to cool; pour off the mother liquor from the crystals that form, evaporate this liquor *a little further over a very low flame* (see Note), and let it cool. Collect the two crops of crystals of oxalic acid, and dry them by pressure between calico.

About 4 grams of oxalic acid, sufficient to fill about one-eighth of a test-tube, should be obtained.

NOTE.—In evaporating the aqueous solution of oxalic acid the flame must be lowered as the solution becomes less in bulk; if the sides of the basin above the liquid are directly heated by the flame some of the acid will be decomposed. Oxalic acid is easily decomposed by heat.

Experiment II.—*Preparation of oxalic acid, and barium sulphate, by the interaction of diluted sulphuric acid and barium oxalate.*

Barium oxalate is nearly, and barium sulphate is quite, insoluble in water; oxalic acid, as you know from the results of the last experiment, can be crystallised from water.

Barium oxalate is caused to react with sulphuric acid in presence of water; the oxalic acid that is produced dissolves in the water, and the other product of the reaction, namely, barium sulphate, remains as a solid. There is difficulty in carrying the reaction to completion because the solid particles of barium sulphate coat the particles of barium oxalate and prevent contact between the oxalate and the sulphuric acid. The quantities of the barium oxalate and sulphuric acid are arranged so that the reaction is just completed, and no excess of either of these compounds remains over; if any sulphuric acid remains over a reaction will occur between this acid and the oxalic acid, when the liquid is evaporated, which will result in the decomposition of some, or it may be of the whole, of the oxalic acid; if any barium oxalate remains over a little of this will pass into solution, and will be obtained mixed with the oxalic acid which crystallises from the evaporated liquid.

Place the moist barium oxalate prepared in *Experiment I., Lesson XXIII.* (p. 110), in a basin about 8 inches diameter, add eight or ten test-tubesful of water, and about three and a half test-tubesful of dilute sulphuric acid (one part acid to ten parts water); heat to boiling, *stirring constantly*; keep boiling for ten or fifteen minutes (two Bunsen lamps may be required), adding a little water from time to time to take the place of that removed by evaporation. The boiling must continue for some time, else the solid barium sulphate formed will coat the particles of barium oxalate, so that the reaction will not be completed. Let the solid settle; pour off a little of the liquid into a test-tube; test a portion of the clear liquid for sulphuric acid, by adding solution of barium nitrate;—if a white precipitate forms, and this

precipitate does not dissolve in dilute hydrochloric or nitric acid, sulphuric acid is present (*Compare testing for a sulphate*, p. 55); test another portion of the clear liquid for a barium compound by adding a few drops of dilute sulphuric acid, which precipitates white barium sulphate insoluble in acids from a solution containing a compound of barium.

If the solution is quite free from sulphuric acid and contains a barium compound, this means that all the sulphuric acid that was added at the beginning of the process has entered into reaction, and that some barium oxalate remains unchanged; in this case add a *little* dilute sulphuric acid (about one-tenth of a test-tubeful) to the contents of the basin, boil, *with constant stirring*, for about five minutes, adding a little water as the boiling proceeds, and then repeat the testing for sulphuric acid and a compound of barium in small portions of the liquid poured off from the solid in the basin. Should the first testing show the presence of a distinct quantity of sulphuric acid, and the absence of a barium compound, in the liquid poured off from the barium sulphate in the basin, this means that the quantity of sulphuric acid added has been more than enough to decompose all the barium oxalate used; in this case add a *very little* solid barium oxalate to the contents of the basin, boil for about five minutes, *with constant stirring*, and addition of a little water to make up for that removed by evaporation, and then repeat the testing for sulphuric acid and a barium compound in small portions of the liquid poured off from the barium sulphate in the basin.

Proceed as directed—adding either a *very little* sulphuric acid or a *very little* barium oxalate, boiling for about five minutes, pouring off, and testing—until the filtered liquid is found to be free from barium compounds, and to contain either no sulphuric acid, or only such a very small quantity of this acid as suffices to produce merely a *faint turbidity* when a few drops of barium nitrate are added, to half a test-tubeful of the liquid. Now pour the whole of the liquid in the basin through a filter, keeping as much as possible of the solid in the basin, wash the barium sulphate in the basin by decantation with hot water three or four times, add the washings to the filtrate, and evaporate (see *Note* on p. 124) till a little of the liquid cooled in a test-tube

deposits white crystals; then let the liquid get quite cold; pour off the mother liquor from the white crystals which separate; evaporate this liquid a *little further*, and let it cool. Collect the two crops of crystals, and press them between calico until quite dry.

About 15 grams (say three-fourths of a test-tubeful) of oxalic acid should be obtained.

NOTE.—In evaporating the aqueous solution of oxalic acid the flame must be lowered as the solution becomes less in bulk; if the sides of the basin above the liquid get directly heated by the flame some of the acid will be decomposed.

LESSON XXVII

INTERACTIONS OF ACIDS AND SALTS *-continued.* THE
OCCURRENCE OF SECONDARY REACTIONS

Apparatus and materials required.—Potassium iodide. Potassium oxalate. Sodium carbonate. Zinc. Starch. Potassium dichromate. Lime water. Ferrous sulphate. Flask of about 5 oz. capacity with good cork fitted with funnel-tube and exit-tube to dip into water in a beaker. Some pieces of ordinary-sized glass tubing and caoutchouc tubing to connect these. Two pinchcocks. Calico. Platinum wire. Slips of wood.

In *Lessons XXIV*, *XXV*, and *XXVI*, you examined various instances of normal reactions between acids and salts, that is, reactions in each of which only a new acid and a new salt are produced. The interaction of an acid and a salt sometimes results in the formation of other substances besides the normal products of the interaction, and in some cases the new acid cannot be isolated because if it is produced it is instantly decomposed into two or more other substances. In this lesson you will examine some interactions between acids and salts wherein secondary reactions take place.

Experiment I. —*To examine the reaction between sulphuric acid solution and the salt potassium iodide.*

The normal products of this reaction are the salt potassium sulphate and the acid hydriodic acid (compare the interaction of potassium chloride and sulphuric acid, p. 114); potassium sulphate is a white solid, and hydriodic acid is a colourless gas very soluble in water.

Arrange an apparatus as shown in figure 80, using a flask of about 150 c.c. (about 5 oz.) capacity and putting about 100 c.c. (say, three test-tubesful) of water into the beaker. Place somewhat less than a fourth of a test-tubeful of potassium iodide

in the flask, and pour about a couple of test-tubesful of a cold mixture of sulphuric acid with about its own volume of water

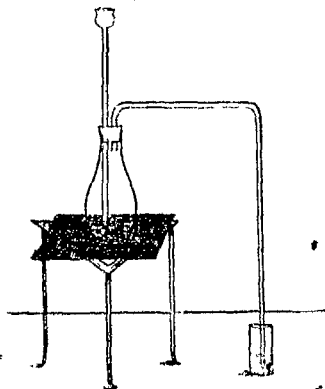


FIG. 11

down the funnel tube. Warm the contents of the flask, gradually raising the temperature to the boiling-point, and keep the liquid boiling for some minutes. Brownish violet solid matter forms in the neck of the flask and in the exit-tube, and a brown colour is probably imparted to the water in the beaker.

Remove the flask from the tripod and allow it to cool somewhat; take out the cork and smell the gas that is coming off; the odour of

sulphuretted hydrogen, and probably also that of sulphur dioxide (smell of burning sulphur), will likely be apparent:

Now dip a piece of blue litmus paper into the liquid in the beaker; the paper is reddened. To a little of the liquid, in a test-tube, add powdered sodium carbonate, and prove that carbon dioxide is given off. To another quantity of the liquid, in a tube, add some pieces of granulated zinc, and prove that hydrogen is evolved. The liquid in the beaker certainly contains an acid.

The acid which has dissolved in the water is hydriodic acid, one of the normal products of the interaction you are examining.

Pour the contents of the flask into a basin and add several test-tubesful of water. You will probably notice a few pieces of a yellow solid floating about, besides the dark brown solid whose presence you have remarked already, and which has now settled to the bottom of the basin. Pick out some of the yellow solid, dry it in filter paper, and heat it on the end of a metal spatula, or on a crucible lid; the solid takes fire, and burns with a pale blue flame, while the smell of burning sulphur is apparent. The yellow solid is sulphur.

Pick out some of the brown solid from the basin; dissolve it in water, noticing that it dissolves only slightly and that the solution is faintly coloured; if you add some alcohol to the water the solid will dissolve more easily. Boil some water with a *very small piece* of starch in it till the starch is thoroughly disintegrated; then add a few drops of this thin starch paste to a little of the solution of the dark brown solid; a deep blue colour is produced. The production of this colour with thin starch paste, in a cold liquid, is characteristic of iodine.

The following products of secondary reactions have been obtained in this examination of the interaction of the salt potassium iodide and the acid sulphuric acid: iodine, and probably also sulphur, sulphuretted hydrogen, and sulphur dioxide. Hydriodic acid and the salt potassium sulphate, which are the normal products of the interaction, are also produced; but secondary reactions occur between the hydriodic acid and some of the excess of sulphuric acid used, for you added far more than enough sulphuric acid to react with the weight of potassium iodide taken, and these secondary reactions produce the iodine, sulphur, &c., whose presence you have proved.

Experiment II.—*To examine the reaction between sulphuric acid and the salt potassium oxalate.*

In Lesson XXVI., Experiment II. (p. 122), you found that oxalic acid, and barium sulphate, were produced by boiling a dilute solution of sulphuric acid with an equivalent quantity of barium oxalate. In the present experiment you will find that when an oxalate is heated with a comparatively large quantity of sulphuric acid the gases carbon monoxide and carbon dioxide are produced, along with the sulphate of the metal of the oxalate used.

The following experiment must be conducted very carefully, because of the extremely corrosive action of hot sulphuric acid.

Into a flask of about 150 c.c. (about 5 oz.) capacity insert a caoutchouc cork fitted with two exit-tubes arranged as shown in figure 31; connect the bent exit-tube with a tube which dips into a beaker that will contain about 100 c.c. (say 3 oz.) of water. Both exit-tubes are made in two pieces, which are joined

by caoutchouc tubing on which pinchcocks are placed. Put about half a test-tubeful of potassium oxalate into the flask;

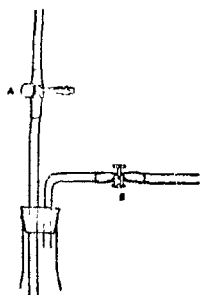


FIG. 31

add about a test-tubeful of concentrated sulphuric acid; close the pinchcock B, and open A, and heat the contents of the flask. After a few minutes gas comes off; bring a lighted taper to the upper end of the straight exit-tube; the gas takes fire and burns with a pale bluish violet flame. This indicates the presence of carbon monoxide.

Now pour a little lime water into the beaker; remove the lamp; open the pinchcock B, and close A. The production of a white precipitate in the lime water shows that carbon dioxide is being given off.

Pour the contents of the flask, when cool, into a basin, and evaporate almost but not quite to dryness over a low flame, *in a good draught place*; allow to cool, and pour off the liquid from the solid that has formed; dissolve the solid in a little water; and crystallise, by evaporating a little and allowing to cool. Pour away the liquid; press the solid in calico till it is dry; re-crystallise from water; dry the solid that separates, and prove it to be (1) a sulphate; and (2) a compound of potassium, by the flame test (see pp. 55, 54).

Oxalic acid is one of the normal products of the interaction of an oxalate and sulphuric acid; but oxalic acid reacts with hot sulphuric acid to produce water, carbon monoxide, and carbon dioxide. As much more sulphuric acid was used in this experiment than would suffice to react with the weight of potassium oxalate taken, the excess of sulphuric acid decomposed the oxalic acid as quickly as it was produced in the primary reaction.

Experiment III.—*To examine the reaction between diluted nitric acid and the salt sodium carbonate.*

Place a little sodium carbonate in a test-tube, add a little diluted nitric acid, and prove (by the lime water test) that carbon

dioxide is being given off. When the reaction slackens, add more nitric acid; then evaporate the liquid, in a basin *in the draught place*, nearly to dryness; recrystallise the solid that separates, twice, from water, as directed in the last experiment; dry the crystals that separate, and prove that the solid thus obtained is a nitrate by the ferrous sulphate test (see p. 70); also prove that the solid is a sodium compound, by holding a *very small* piece of it, on a *clean* platinum wire, in a Bunsen flame, and noticing the deep yellow colour which is imparted to the flame.

Judging from the results of other experiments on the interactions between acids and salts, you would expect the interaction examined in the present experiment to produce sodium nitrate and an acid (carbonic acid). But carbonic acid has not been isolated; if it is produced in any reaction, it at once decomposes into water and carbon dioxide.

Experiment IV.—*To examine the reaction between sulphuric acid and the salt potassium dichromate.*

The normal products of this reaction would be the salt potassium sulphate and dichromic acid. It will suffice for the present purpose to prove that something is produced which is not one of the *normal* compounds, without inquiring whether the normal products are or are not also formed.

Put about a test-tubeful of powdered potassium dichromate into a flask of about 100 to 120 c.c. (about 3 to 4 oz.) capacity; add a couple of test-tubeful of conc. sulphuric acid, and heat gradually. As the liquid becomes hot a visible reaction begins; when the reaction is proceeding fairly vigorously remove the lamp, and bring a smouldering splint of wood into the neck of the flask. The smouldering splint bursts into flame; hence you conclude that oxygen is coming off. More accurate experiments confirm this conclusion.

This experiment must be conducted carefully, because of the extremely corrosive action of hot sulphuric acid.

LESSON XXVIII

PREPARATION OF AQUEOUS SOLUTIONS OF ALKALIS, AND
SOME REACTIONS OF THESE SOLUTIONS

Apparatus and materials required.—Sodium carbonate crystals. Lime (in lumps). Ammonium chloride, ammonium sulphate, and ammonium nitrate. Solutions of ferric chloride, manganese sulphate, mercuric chloride, copper sulphate, and zinc sulphate. Solid caustic soda. Olive oil. Soap. Common salt. Alcohol. Methyl orange solution. Large basin (about 8 inches diameter). Small apparatus to make carbon dioxide. Flask, about 9 oz., fitted with cork carrying a funnel tube and exit-tube to pass into water. Burette, and clamp. Pipettes to contain 5 c.c., 25 c.c., and 50 c.c. respectively. Two small flasks (about 2 oz.). Short piece of glass tubing.

In *Lessons XI.*, *XII.*, and *XIII.* you examined some of the typical reactions of acidic and basic oxides. Certain basic oxides combine with water to form hydroxides which are classed together as *alkalis*. The alkalis that are used most frequently in the laboratory are caustic potash and caustic soda; a solution of ammonia in water (probably containing the compound ammonium hydroxide) is also much used as an alkali. In *Lessons XXI.* and *XXII.* you used the reactions of the alkalis potash and ammonia with the salts lead nitrate, copper chloride, and iron sulphate, to prepare the oxides of lead, copper, and iron. In this lesson we shall examine the preparation of solutions of caustic soda and ammonia, and some of the reactions of these solutions.

Experiment I.—*Preparation of a solution of caustic soda from sodium carbonate.*

A fairly dilute boiling solution in water of sodium carbonate reacts with slaked lime, to produce calcium carbonate which is nearly insoluble

in water, and caustic soda which remains in solution in the water. As long as there is any unreacted sodium carbonate present the solution will give off carbon dioxide when it is acidified. If less water is present than (roughly) about four to five times the weight of crystallised sodium carbonate used, the chemical change is reversed and the caustic soda and calcium carbonate interact to re-form lime and sodium carbonate.

Dissolve about 108 grams (say five and a half test-tubesful) of powdered crystallised sodium carbonate in about 500 c.c. (say 17 oz.) of ordinary water in a large basin, and add about 60 grams (say four test-tubesful) of powdered lime shaken with about 200 c.c. (about seven test-tubesful) of ordinary water; a lump of lime must be powdered for the purpose, as, if the lime that is used has been kept in powder for some time, it will contain a good deal of calcium carbonate. Boil for about fifteen minutes, stirring frequently with a glass rod, and adding three or four test-tubesful of water from time to time during the boiling, to replace the water removed as steam. Then let the solid matter settle slightly; pour a little of the supernatant liquid through a filter into a test-tube, and to this liquid add hydrochloric acid: if carbon dioxide (a gas which produces a white solid in lime water) is not given off the reaction is finished; but if carbon dioxide is given off continue to boil the contents of the basin (adding a little water every five minutes or so) until a little of the filtered supernatant liquid does not give off carbon dioxide when it is acidified by hydrochloric acid.

When the reaction is finished allow the solid matter to settle for a few minutes, decant the supernatant liquid into another basin, and then pour it through a calico filter into a bottle, and cork the bottle; the liquid, which is a solution of caustic soda, will be used in the following experiments.

Transfer a little of the solid matter from the basin to a test-tube, add diluted hydrochloric acid, and prove that carbon dioxide is given off—that is to say, prove that the solid is a carbonate: to the solution of this solid in hydrochloric acid which remains in the test-tube, after filtering from undissolved solid matter if the whole has not dissolved, add ammonia solution until you smell ammonia when the tube is shaken, then add acetic acid until the

liquid is acid to litmus paper, and then add a solution of ammonium oxalate; the formation of a white precipitate (which is calcium oxalate) proves the presence of a compound of calcium.¹ The solid matter in the basin is, therefore, calcium carbonate.

Experiment II.—*To observe the interaction of caustic soda solution and carbon dioxide.*

Set up a small apparatus for making carbon dioxide, as shown in figure 82, putting broken marble into the bottle, and pouring diluted hydrochloric acid down the funnel tube; allow the gas to pass downwards into a dry test-tube (see the figure), until a lighted taper is at once extinguished when it is brought close to the mouth of the tube.

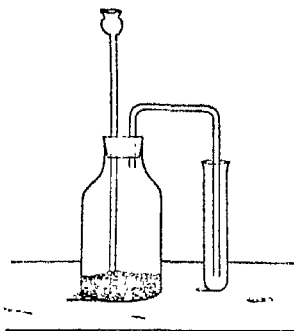


FIG. 82

While the test-tube is being filled with carbon dioxide pour about 100 c.c. (three test-tubesful) of the solution of caustic soda you made in *Experiment I.* into a small basin.

When the test-tube is quite full of carbon dioxide pour into it enough of the caustic soda solution in the basin to occupy about one-eighth of the tube;

at once cover the mouth of the tube with the thumb, shake vigorously, and then bring the mouth of the tube (still closed by the thumb) under the solution of caustic soda in the basin, and remove the thumb. Shake the tube cautiously, taking care that no gas escapes from it. The rise of the caustic soda solution in the test-tube indicates that the carbon dioxide is being absorbed by the solution. To confirm this indication, allow the carbon

¹ A characteristic reaction of compounds of calcium in solution is that they react with a solution of an oxalate to produce white calcium oxalate, a salt which is insoluble in acetic acid, but dissolves in hydrochloric or nitric acid; ammonia was added in your experiment to convert the hydrochloric acid which was present in the solution into ammonium chloride, for had the hydrochloric acid been left in the solution it would have prevented the precipitation of calcium oxalate.

dioxide which is coming off from the marble and hydrochloric acid to pass, for a minute or two, into about a sixth of a test-tubeful of the caustic soda solution you made in the last experiment; then remove the apparatus from which carbon dioxide is being given off, add hydrochloric acid to the liquid in the tube, and prove that the gas which is evolved is carbon dioxide.

Carbon dioxide combines with caustic soda to form sodium carbonate. This reaction, namely, combination with carbon dioxide, is common to the alkalis as a class.

Experiment III.—*Interaction of caustic soda solution with ammonium salts. Preparation of an aqueous solution of ammonia.*

To small quantities of solid ammonium chloride, ammonium sulphate, and ammonium nitrate, in test-tubes, add about 10 c.c. of the solution of caustic soda prepared in *Experiment I.*, heat the contents of each tube nearly to boiling, and cautiously smell the gas that is given off. The gas is ammonia.

Ammonium compounds react with alkalis to give off ammonia.

Arrange an apparatus as shown in figure 33, using a flask of about 100 c.c. (say 3¹/₂ oz.) capacity, and putting about 150 c.c. of water in the beaker. Place 8 grams (about quarter a test-tubeful) of ammonium chloride in the flask, add about a couple of test-

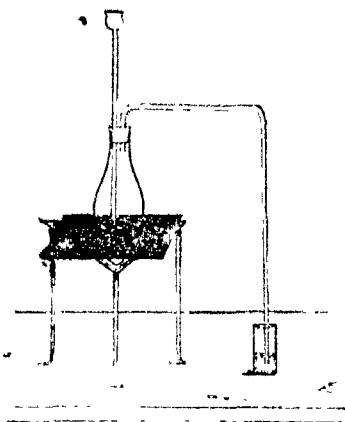


FIG. 33

tubeful of the solution of caustic soda prepared in *Experiment I.*, and heat the flask over a low flame. The reaction soon begins; ammonia gas is given off, and is dissolved in the water in the beaker. Gradually heat the liquid in the flask to boiling, and continue to boil for about ten or fifteen minutes; then remove

the flask before you extinguish the lamp, to prevent any chance of the running back of the liquid in the beaker into the flask.

Keep the solution of ammonia you have made, for use in the next experiment, except about quarter a test-tubeful, into which quantity pass carbon dioxide for some minutes, and then prove that when the liquid is acidified it gives off carbon dioxide (see *Experiment II.*).

Ammonium carbonate is produced in this reaction, as sodium carbonate was formed in the corresponding reaction of carbon dioxide with caustic soda.

Experiment IV.—*To observe the reactions of caustic soda and ammonia solutions with solutions of various salts.*

Compare the preparations, in *Lesson XXI.*, of some metallic oxides from their salts by causing solutions of these salts to interact with alkali solutions.

Arrange ten clean tubes in a test-tube stand. Pour a few c.c. of the following solutions, in water, into these tubes in the order directed. Into tubes 1 and 2 put solution of ferric chloride, into tubes 3 and 4 solution of manganese sulphate, into tubes 5 and 6 solution of copper sulphate, into tubes 7 and 8 solution of mercuric chloride, and into tubes 9 and 10 solution of zinc sulphate. Into each alternate tube, beginning with the first, pour a *very little* of the caustic soda solution prepared in *Experiment I.*; and into each alternate tube, beginning with the second, pour a *very little* of the ammonia solution prepared in *Experiment III.* Shake each tube, and note what visible change has occurred. Now nearly fill each tube with the same solution which you have already added to it; again mix the contents of each tube, and note the visible changes that occur.

The precipitates produced are hydroxides of the metals of the salts used, except in the case of mercuric chloride, where the precipitate is an oxide of mercury.

The formation of metallic hydroxides, or oxides, by the interaction of solutions of alkalis and metallic salts, furnishes a method for preparing metallic oxides which is very often used in the laboratory.

Experiment V.—*Interaction of caustic soda solution with a liquid fat. SAPONIFICATION.*

Soaps are made by boiling fat with solutions of caustic soda or caustic potash. The fats are mixtures of compounds the constituents of which are glycerin and various fatty acids; caustic potash, and caustic soda, react with these compounds to produce glycerin, and the potassium, or sodium, salts of the fatty acids which were in combination with the glycerin; and these potassium, and sodium, salts of fatty acids are soaps. Soap is nearly insoluble in a saturated solution of common salt. The interaction between a caustic alkali and a fat is called *saponification*; the reaction goes most quickly when an alcoholic solution of the alkali and a liquid fat, are employed.

Dissolve a stick of caustic soda about an inch in length in about three-quarters of a test-tubeful of alcohol, by warming carefully over a low flame; add about 20 or 30 drops of olive oil, boil for about three minutes, and pour the liquid into about three or four test-tubeful of a saturated solution of common salt in a beaker.

After a little time pale buff-coloured semi-solid matter rises towards the top of the salt solution; this is the soap produced in the reaction; the glycerin remains in solution in the liquid.

ADDENDUM TO EXPERIMENT V.—*Comparison of the volumes of the same solution of soap required to produce lathers in equal volumes of distilled and hard waters.*

It is advisable to perform an experiment at this stage to illustrate the actions of hard and soft waters on soap. These reactions will not, however, be gone into here; they will be understood better at a later part of the course. Suppose a soap to be pure potassium stearate, and let it be added to a water which is hard from the presence of calcium carbonate; the normal reaction between two salts takes place (see Lesson XXII.), and two new salts, potassium carbonate and calcium stearate, are formed; when the whole of the calcium carbonate in the water has reacted with the soap, then, but not till then, is there any unchanged soap present, and only then, therefore, is a lather produced.

Cut a small piece of soap into shreds and dissolve the shreds in alcohol by shaking and warming gently; let the liquid stand for a short time, and then decant the clearer upper portion through a filter. Pour a test-tubeful of distilled water into a small flask,

and a test-tubeful of hard water¹ into another similar flask. Draw out a piece of glass tubing to an opening so fine that when you suck up some of the solution of soap into the tube the liquid flows from the narrowed end in drops which can be counted. Allow one or two drops of the solution of soap to flow into the distilled water; shake the flask vigorously, and notice if the lather that is produced remains on the surface of the water for, say, ten seconds. Count the number of drops of the solution of soap that are needed to produce a lather which is permanent for the time mentioned. Now find how many drops of the solution of soap must be added to the hard water in order to produce a lather that is permanent for ten seconds. Considerably more of the soap solution will be required to produce a lather in the hard water than is needed to effect the same result in the soft (distilled) water.

Experiment VI.—*Comparison of the volumes of the same solution of caustic soda required to neutralise different volumes of the same diluted hydrochloric acid.*

Alkalis neutralise acids, forming salts. Solutions of acids, as you know, change the colour of litmus from blue to red, and solutions of alkalis change the colour of reddened litmus to blue. (These facts were used in *Lessons XI., XII., and XIII.*, in your examination of the interactions of acidic and basic oxides.) Solutions of acids produce a rose-pink colour, and solutions of alkalis a yellow-brown colour, in a solution of methyl orange.

Dilute about a test-tubeful of concentrated hydrochloric acid with about ten times its volume of water, *taking care to mix the water and the acid solution thoroughly.* Withdraw, by means of pipettes (see p. 155), 5 c.c., 25 c.c., and 50 c.c., of this much diluted hydrochloric acid, and put these quantities of the liquid into three *clean* beakers; then add to each liquid a little water and five or six drops of a dilute solution of methyl orange.

Now rinse a *clean* burette (see p. 154) with a *very* little of the solution of caustic soda prepared in *Experiment I.*, and let the liquid run out of the burette; then fill the burette with the

¹ If the tap water is not hard, shake a little powdered chalk into it, pass carbon dioxide into the liquid for about ten or fifteen minutes, and filter; some of the calcium carbonate will dissolve and hard water will be formed.

solution of caustic soda, and keep the pinchcock open until the level of the liquid has fallen to the zero point of the graduations of the burette. Now run the soda solution, drop by drop, from the burette into the 5 c.c. of the diluted hydrochloric acid, shaking the beaker while the soda solution drops into it. When you notice the production for a moment of a yellow colour in the wake of each drop of the soda solution, add the solution from the burette very cautiously, *one drop at a time*, until the rose-pink colour of the liquid in the beaker changes to a brownish red tint, stopping before a yellow shade is produced. The whole of the hydrochloric acid has now reacted with the caustic soda, to produce sodium chloride and water, and the liquid contains neither acid nor alkali; it is neutral.

Read off, accurately, the volume of the caustic soda solution used. Then exactly neutralise, with the soda solution in the burette, the 25 c.c. of the diluted hydrochloric acid solution you placed in a beaker at the beginning of this experiment, and read off the volume of the soda solution used. Finally neutralise the 50 c.c. of diluted hydrochloric acid solution you have already measured off with the same soda solution as before, and note the volume of the soda solution required.

If your experiments have been conducted carefully and accurately, they show that 25 c.c. of the diluted hydrochloric acid solution have required for neutralisation a volume of the caustic soda solution equal to five times that required by 5 c.c. of the hydrochloric acid solution, and that the volume of the solution of caustic soda used to neutralise 50 c.c. of the hydrochloric acid solution is ten times the volume required to neutralise 5 c.c. of the same acid solution.

The results of Experiment VI. show that the ratio between the weights of caustic soda and hydrochloric acid which react in solution to produce a neutral liquid is constant.

ADDENDUM TO SECTION I. OF PART I. OF ELEMENTARY COURSE

It will be useful to classify the methods of formation and preparation, and the principal reactions, of the elements and compounds that have been dealt with in this part of the course; to indicate some other substances that may be prepared by similar reactions, and that interact similarly to the substances that have been considered; and to note those reactions which have been employed as qualitative tests for detecting the presence of certain elements or classes of compounds.

The Student is urged to refer to the experiments he has made in each example in the following list, to consider these experiments carefully, and to compare them with the other examples under the same heading, in order that he may thoroughly grasp the significance of the various general reactions of each class of substances.

A. Classification of Methods of Formation and Preparation of Elements and Compounds dealt with in the foregoing Lessons

I. Oxides

(i.) BY THE DIRECT COMBINATION OF OXYGEN WITH THE OTHER ELEMENT

<i>Oxide</i>	<i>Method of Formation</i>	<i>Lesson</i>	<i>Experiment</i>	<i>Page</i>
Water	By burning hydrogen in air	X.	I.	47
Water	By heating red lead in hydrogen	X.	II.	49
Phosphorus oxide	By burning phosphorus in air	VII.	II. and III.	28-30
Magnesia	By burning magnesium in air	V.	I.	20
Ferrioxide (rust)	By rusting iron in moist air	VII., VIII., IX.	I. in each lesson	27, 34, 41
Lead monoxide (litharge) and red lead	By heating lead in air	V.	II.	22

(ii.) BY HEATING HYDROXIDES WHICH ARE PRECIPITATED BY
ADDING ALKALIS TO SOLUTIONS OF SALTS OF THE
METALS OF THE OXIDES

Oxide	Method of Formation	Element	Experiment	Page
Lead monoxide	Potash added to solution of lead nitrate; pp. heated	XXI.	I.	102
Ferric oxide	Ammonia added to solution of ferric sulphate; pp. heated	XXII.	I.	105
Magnetic oxide of iron	Ammonia added to mixture of solutions of ferric and ferrous sulphates	XXII.	II.	106
Copper oxide	Potash added to boiling solution of copper chloride	XXI.	II.	103

The method of precipitating a hydroxide, and decomposing the dried precipitate by heat into oxide and water, is very often employed for preparing the oxides of metals. *Additional examples:*—Oxides of aluminium, bismuth, chromium, and zinc.

(iii.) FROM ANOTHER OXIDE OF THE SAME ELEMENT

Oxide	Method of Formation	Element	Experiment	Page
Lead peroxide	By the reaction of diluted nitric acid with red lead	XVII.	II.	82
Nitrogen dioxide	By adding oxygen to nitric oxide	XV.	I.	69

Peroxides are generally prepared by adding oxygen to an element or to an oxide containing less oxygen than the peroxide required; this addition of oxygen is generally accomplished by a reaction between the element, or the lower oxide, and some compound which readily parts with oxygen. *Additional examples:*—Stannic oxide, by heating tin with nitric acid; barium peroxide, by reaction of a barium salt in solution with an alkali and hydrogen peroxide.

(iv.) BY THE INTERACTION OF AN ELEMENT WITH AN ACID
WHEREBY OXYGEN IS REMOVED FROM THE ACID

Oxide	Method of Formation	Element	Experiment	Page
Nitric oxide	By the reaction of copper with nitric acid	XV.	I.	68

Some of the oxides of non-metals are prepared by heating the non-metals with nitric acid, the oxygen removed from the acid combining with the non-metal. *Examples*:—Oxides of iodine and phosphorus.

(v.) BY THE INTERACTION OF A SALT WITH AN ACID

<i>Oxide</i>	<i>Method of Formation</i>	<i>Lesson</i>	<i>Experiment</i>	<i>Page</i>
Carbon dioxide	By the action of diluted nitric acid on sodium carbonate	XXVII.	III.	129
Carbon monoxide	By the action of conc. sulphuric acid on potassium oxalate	XXVII.	II.	128

Additional example:—Silicon oxide (silica), by the action of hydrochloric acid on a silicate.

II. Salts

(i.) BY THE COMBINATION OF ACIDIC AND BASIC OXIDES

<i>Salt</i>	<i>Method of Formation</i>	<i>Lesson</i>	<i>Experiment</i>	<i>Page</i>
Potassium sulphate	By combination of potassium oxide with sulphur trioxide, in aqueous solution	XI.	I.	53
Zinc sulphate	By dissolving zinc oxide in an aqueous solution of sulphur trioxide	XII.	I.	57

(ii.) BY THE COMBINATION OF A METAL WITH A
NON-METAL

<i>Salt</i>	<i>Method of Formation</i>	<i>Lesson</i>	<i>Experiment</i>	<i>Page</i>
Mercury iodide	By rubbing mercury with iodine in presence of a very little alcohol	III.	I.	14

Method (i.) or (ii.) may be employed in the preparation of many salts; for instance, the sulphates of calcium, chromium, copper, iron, and magnesium; the nitrates of calcium, copper, iron, and magnesium; the chlorides of copper, iron, lead, mercury, and tin; the sulphides of copper, iron, lead, mercury, and tin; the carbonates of calcium, magnesium, potassium, and sodium.

(iii.) BY THE INTERACTION OF AN ACID AND A METAL

Salt	Method of Formation	Lesson	Experiment	Page
Zinc sulphate	By dissolving zinc in diluted sulphuric acid	XIV.	I.	63
Tin chloride	By dissolving tin in conc. hydrochloric acid	XIV.	II.	65
Lead chloride	By dissolving lead in conc. hydrochloric acid	XVI.	II.	74
Lead nitrate	By dissolving lead in diluted nitric acid	XX.	I.	98
Copper nitrate	By dissolving copper in diluted nitric acid	XV.	I.	68
Ferrous sulphate	By dissolving iron in diluted sulphuric acid	XIX.	I.	93

(iv.) BY THE INTERACTION OF AN ACID WITH A BASIC METALLIC OXIDE

Salt	Method of Formation	Lesson	Experiment	Page
Lead chloride	By dissolving lead monoxide in diluted hydrochloric acid	XVI.	III.	76
Copper chloride	By dissolving copper oxide in diluted hydrochloric acid	XX.	II.	100
Copper nitrate	By dissolving copper oxide in diluted nitric acid	XVI.	I.	73

Methods (iii.) and (iv.) are much used for the preparation of salts; for instance, the sulphates and nitrates of barium, calcium, chromium, iron, magnesium, mercury, potassium, sodium, and tin; the chlorides of barium, calcium, mercury, potassium, sodium, and tin.

(v.) BY THE INTERACTION OF AN ACID WITH A SALT

Salt	Method of Formation	Lesson	Experiment	Page
Potassium sulphate	By heating potassium chloride with conc. sulphuric acid	XXIV.	I.	114
Potassium sulphate	By heating potassium iodide with sulphuric acid	XXVII.	I.	125
Potassium sulphate	By heating potassium oxalate with sulphuric acid	XXVII.	II.	128
Lead sulphate	By heating lead nitrate with conc. sulphuric acid	XXV.	I.	118
Barium sulphate	By heating barium oxalate with diluted sulphuric acid	XXVI.	II.	122
Ferrous sulphate	By heating ferrous sulphate with sulphuric acid, in presence of oxygen	XIX.	II.	95
Sodium nitrate	By heating sodium carbonate with nitric acid	XXVII.	III.	129

This method is of very general applicability. Most sulphates and nitrates, and many chlorides, can be prepared by heating carbonates with sulphuric, nitric, or hydrochloric acid.

(vi.) BY THE INTERACTION OF A SALT WITH ANOTHER SALT

<i>Salt</i>	<i>Method of Formation</i>	<i>Lesson</i>	<i>Experiment</i>	<i>Page</i>
Potassium nitrate, and lead iodide	By mixing aqueous solutions of potassium iodide and lead nitrate	XXIII.	II.	111
Barium oxalate, and potassium nitrate	By mixing aqueous solutions of barium nitrate and potassium oxalate	XXIII.	I.	109

This method is much used for preparing salts. The salts formed in the reaction are separated from one another, and from excess of the salts that have been caused to react, by taking advantage of differences in the solubilities (generally in water) of these salts.

• III. Acids

BY THE REACTION OF A SALT WITH AN ACID

<i>Acid</i>	<i>Method of Formation</i>	<i>Lesson</i>	<i>Experiment</i>	<i>Page</i>
Hydrochloric acid in aqueous solution	By heating potassium chloride with conc. sulphuric acid, and leading the gaseous acid produced into water	XXIV.	I.	114
Nitric acid	By heating lead nitrate with conc. sulphuric acid, and condensing the gaseous acid produced by cooling it	XXV.	I.	117

The method illustrated by these two preparations is fairly general for preparing volatilisable acids.

<i>Acid</i>	<i>Method of Formation</i>	<i>Lesson</i>	<i>Experiment</i>	<i>Page</i>
Oxalic acid	By passing sulphydric acid gas into water in which lead oxalate is suspended	XXVI.	I.	120
Oxalic acid	By heating barium oxalate with the proper quantity of diluted sulphuric acid	XXVI.	II.	122

The method illustrated by these two preparations is fairly general for preparing acids that cannot be volatilised, but can be crystallised from water.

IV. Alkalies

BY THE INTERACTION OF AN AQUEOUS SOLUTION OF A SALT OF THE ALKALI METAL WITH ANOTHER ALKALI

<i>Alkali</i>	<i>Method of Formation</i>	<i>Lesson</i>	<i>Experiment</i>	<i>Page</i>
Caustic soda; in aqueous solution	By boiling sodium carbonate with slaked lime	XXVIII.	I.	131
Ammonia; in aqueous solution	By boiling ammonium chloride with solution of caustic soda, and leading the gaseous ammonia into water	XXVIII.	III.	133

This is the method generally used for preparing alkalis.

V. Elements

(i.) BY REMOVING OXYGEN FROM AN OXIDE OF THE ELEMENT

<i>Element</i>	<i>Method of Formation</i>	<i>Lesson</i>	<i>Experiment</i>	<i>Page</i>
Lead	By heating red lead in hydrogen	X.	II.	50

This method is applicable for preparing several metals; for instance, bismuth, copper, iron, platinum, silver, tin, and zinc.

(ii.) BY HEATING OXIDES OR SALTS

<i>Element</i>	<i>Method of Formation</i>	<i>Lesson</i>	<i>Experiment</i>	<i>Page</i>
Oxygen	By heating red lead, or oxide of mercury	V.	III., IV.	23, 25
Oxygen	By heating potassium chlorate	VIII.	II.	37

(iii.) FROM ACIDS BY THE ACTION OF METALS

<i>Element</i>	<i>Method of Formation</i>	<i>Lesson</i>	<i>Experiment</i>	<i>Page</i>
Hydrogen	By the action of zinc, magnesium, or iron, on diluted hydrochloric or sulphuric acid	IX.	II.	12

Methods (ii.) and (iii.) are special methods for oxygen and hydrogen.

B. Classification of Reactions of Elements, Oxides, Acids, Salts, and Alkalis examined in the foregoing Lessons

I. Elements

(i.) HEATED IN AIR OR OXYGEN FORM OXIDES

<i>Element</i>	<i>Reaction</i>	<i>Lesson</i>	<i>Experiment</i>	<i>Page</i>
Hydrogen	Burnt in air forms water	X.	I.	47
Phosphorus	Burnt in air forms phosphorus oxide	VII.	II. and III.	28, 30
Magnesium	Burnt in air forms magnesia	V.	I.	20
Lead	Heated in air forms litharge and red lead	V.	II.	22
Iron	Exposed to moist air forms rust	VII, VIII, IX.	I. in each Lesson.	27, 34, 41

(ii.) METALS REACT WITH ACIDS, FORMING SALTS, AND USUALLY (BUT NOT ALWAYS) GIVING OFF HYDROGEN

<i>Element</i>	<i>Reaction</i>	<i>Lesson</i>	<i>Experiment</i>	<i>Page</i>
Zinc, magnesium, or iron	Dissolved in diluted sulphuric acid gives off hydrogen, and produces zinc, magnesium, or iron sulphate	IX.	II.	42
Tin	Dissolved in conc. hot hydrochloric acid gives off hydrogen, and forms tin chloride	XIV.	II.	65
Iron	Dissolved in diluted sulphuric acid gives off hydrogen, and forms iron sulphate	XIX.	I.	93
Copper	Dissolved in diluted nitric acid gives off nitric oxide, and forms copper nitrate	XV.	I.	68
Lead	Dissolved in diluted nitric acid gives off nitric oxide, and forms lead nitrate	XX.	I.	98

II. Oxides

(i.) BASIC OXIDES REACT WITH ACIDS TO FORM SALTS AND WATER

Oxide	Reaction	Lesson	Experiment	Page
Potassium oxide	Neutralised by diluted sulphuric acid forms potassium sulphate	XI.	I.	53
Zinc oxide	Dissolved in diluted sulphuric acid forms zinc sulphate	XII.	I.	57
Lead monoxide	Dissolved in diluted hydrochloric acid forms lead chloride	XVI.	III.	76
Copper oxide	Dissolved in diluted hydrochloric acid forms copper chloride	XX.	II.	100
Copper oxide	Dissolved in diluted nitric acid forms copper nitrate	XVI.	I.	73

This reaction is general for all basic oxides.

(ii.) METALLIC PEROXIDES REACT WITH CONC. SULPHURIC ACID TO FORM SALTS (SULPHATES), WATER, AND OXYGEN; AND WITH HYDROCHLORIC ACID TO FORM SALTS (CHLORIDES), WATER, AND CHLORINE

Oxide	Reaction	Lesson	Experiment	Page
Lead peroxide	Heated with hydrochloric acid forms lead chloride, and gives off chlorine	XVII.	III.	85

These reactions are general for metallic peroxides, whether basic or acidic.

III. Acids

(i.) REACT WITH METALS TO FORM SALTS, AND GENERALLY ALSO HYDROGEN

Acid	Reaction	Lesson	Experiment	Page
Diluted sulphuric acid	Dissolves zinc, giving off hydrogen, and forming zinc sulphate	IX. XIV.	II.	42
			I.	63
Diluted sulphuric acid	Dissolves iron, giving off hydrogen, and forming ferrous sulphate	XIX.	I.	93

(i.) REACT WITH METALS TO FORM SALTS, AND GENERALLY
ALSO HYDROGEN—(continued)

<i>Acid</i>	<i>Reaction</i>	<i>Lesson</i>	<i>Experiment</i>	<i>Page</i>
Conc. hydrochloric acid	Dissolves tin, giving off hydrogen, and forming tin chloride	XIV.	II.	65
Diluted nitric acid	Dissolves copper, giving off nitric oxide, and forming copper nitrate	XV.	I.	68
Diluted nitric acid	Dissolves lead, giving off nitric oxide, and forming lead nitrate	XX.	I.	98

Almost every metal dissolves in some determinate acid, forming a salt or salts, and giving off a gas which is frequently hydrogen.

(ii.) REACT WITH BASIC OXIDES, FORMING SALTS AND
WATER

<i>Acid</i>	<i>Reaction</i>	<i>Lesson</i>	<i>Experiment</i>	<i>Page</i>
Diluted sulphuric acid	With potassium oxide forms potassium sulphate	XI.	I.	53
Diluted sulphuric acid	With zinc oxide forms zinc sulphate	XII.	I.	57
Diluted hydrochloric acid	With lead monoxide forms lead chloride	XVI.	III.	76
Diluted hydrochloric acid	With copper oxide forms copper chloride	XX.	II.	100
Diluted nitric acid	With copper oxide forms copper nitrate	XVI.	I.	73

(iii.) REACT WITH METALLIC PEROXIDES TO FORM SALTS,
WATER, AND CHLORINE IF THE ACID IS HYDROCHLORIC,
OR OXYGEN IF THE ACID IS CONC. SULPHURIC

<i>Acid</i>	<i>Reaction</i>	<i>Lesson</i>	<i>Experiment</i>	<i>Page</i>
Hydrochloric acid	Heated with lead peroxide forms lead chloride and chlorine	XVII.	III.	85

(iv.) REACT WITH SALTS TO FORM OTHER SALTS AND OTHER ACIDS; sometimes Secondary Reactions also occur

Reagent	Reaction	Lesson	Page	Exp.
Conc. sul- phuric acid	With potassium chloride gives potassium sulphate and hydrochloric acid	XXIV.	I.	114
Conc. sul- phuric acid	With lead nitrate gives lead sulphate and nitric acid	XXV	I.	117
Diluted sul- phuric acid	With barium oxalate gives barium sulphate and oxalic acid	XXVI	II.	122
Diluted sul- phuric acid	With potassium iodide gives potassium sulphate, hydrochloric acid, iodine, and also sulphur dioxide	XXVII	I.	125
Diluted nitric acid	With sodium carbonate gives sodium nitrate, water, and carbon dioxide	XXVII	III.	128

IV. Alkalis

Examples of the following reactions are given in *Lesson XXVIII.* (pp. 130-135).

- (i.) REACT WITH SOLUTIONS OF SALTS OF HEAVY METALS TO PRECIPITATE HYDROXIDES (OR SOMETIMES OXIDES) OF THESE METALS, AND TO FORM A SALT OF THE METAL OF THE ALKALI USED.
- (ii.) REACT WITH SALTS OF AMMONIUM TO FORM AMMONIA AND A SALT OF THE ALKALI METAL.
- (iii.) REACT WITH CARBON DIOXIDE TO FORM A CARBONATE OF THE METAL OF THE ALKALI.
- (iv.) NEUTRALISE ACIDS, FORMING SALTS AND WATER.
- (v.) SAPONIFY FATS.

V. Salts

Examples of the following reactions should be written out by the student; he should refer to *Reactions of Acids* (iv.), *Reactions of Alkalis* (i.), and *Preparations of Salts* (vi.), (pp. 147, 142).

- (i.) REACT WITH ACIDS TO FORM OTHER SALTS AND OTHER ACIDS.
- (ii.) REACT WITH ALKALIS TO FORM HYDROXIDES (OR OXIDES) OF THE METALS OF THE SALTS.
- (iii.) REACT WITH OTHER SALTS TO FORM TWO NEW SALTS.

C. Reactions that have been employed as Qualitative Tests for Detecting the Presence of certain Elements or classes of Compounds

<i>Element or Group of Elements detected</i>	<i>Reaction employed as Test</i>	<i>Page</i>
Potassium in its compounds	Non-luminous flame coloured lavender-purple	54, 56
Zinc in its compounds	Solid heated with cobalt nitrate goes green	58
Tin in its compounds	Solution gives grey pp. with mercuric chloride solution	66, 67
Lead in its compounds	Solution gives white pp. with alcohol and dilute sulphuric acid	75
Iron in its compounds	Solid imparts reddish yellow colour to borax bead (See also tests to distinguish a ferrous from a ferric salt in solution)	94, 95 107
Barium in its compounds	Solution gives white pp. with dilute sulphuric acid	123
Copper in its compounds	Solution gives azure blue colour with ammonia	69
Calcium in its compounds	Solution gives white pp. with ammonium oxalate and acetic acid	132, <i>note</i>
Sulphur	Heated, burns with blue flame and smell of sulphur dioxide	126
Iodine	Solution gives blue colour with starch paste	127
Chlorine	Smell; the gas gives blue colour with potassium iodide and starch paste	90, <i>note</i>
Chlorine in its compounds	Solution gives white pp. with nitric acid followed by silver nitrate solution	67
Sulphuric acid and sulphates	Solution gives white pp. with barium nitrate solution preceded by hydrochloric acid	55, 56
Oxalates	Solution acidified by acetic acid, after addition of excess of ammonia, gives white pp. with calcium chloride solution	110
Nitric acid and nitrates	Solution gives brown colour when mixed with conc. sulphuric acid, and solution of ferrous sulphate is added	70
Carbon monoxide gas	Burns with pale blue-violet flame	128
Carbon dioxide gas	Gives white pp. in lime water	8
Hydrogen gas	Very light; burns with almost non-luminous flame	42
Oxygen gas	Kindles a glowing chip of wood	24

See also general reactions for recognising basic oxides, acidic oxides, and peroxides:—*Lesson XI.* (pp. 53–56), and *Lesson XVIII.* (pp. 88–92).

A COURSE OF PRACTICAL CHEMISTRY

PART I ELEMENTARY

SECTION II

Volumetric (or titimetric) estimations of acids, alkalis (including ammonia), alkaline carbonates, iron salts, chlorides, calcium compounds, and iodine.

It is assumed that the student is acquainted with the use of chemical equations, and that he has a fair knowledge of the elementary facts of chemistry, before he begins this section of the course.

The experiments performed in *Lesson XI.* (pp. 53-56) showed that certain definite quantities of sulphur trioxide and potassium oxide react, in aqueous solutions, to produce the salt potassium sulphate. In order to determine when a sufficient quantity of the solution of the basic potassium oxide had been added to the solution of the acidic sulphur trioxide, you made use of the facts : (i.) that an aqueous solution of potassium oxide turns red litmus blue ; (ii.) that an aqueous solution of sulphur trioxide turns blue litmus red ; and (iii.) that an aqueous solution of potassium sulphate--the salt formed by the interaction of the two oxides--does not affect the colour of litmus.

In *Lesson XXVIII., Experiment VI.* (pp. 186, 187), you found that a definite quantity of caustic soda reacted with a definite quantity of hydrochloric acid, both compounds being in solution in water, to produce a solution that was neutral to litmus,

that is, a solution which did not alter the colour of either blue or red litmus; and you also found that when twice as much hydrochloric acid was used twice as much caustic soda was required to react with the acid to produce the solution neutral to litmus; you found that hydrochloric acid and caustic soda react, in aqueous solutions, in definite quantities by weight, to produce a solution that is neutral to litmus.

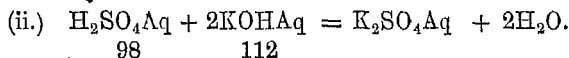
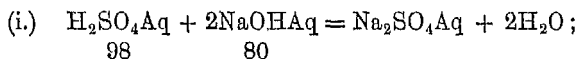
Now, if you weighed out a definite quantity of potassium oxide, or potassium hydroxide, dissolved that in a measured volume of water, mixed the solution thoroughly, withdrew a measured volume of this liquid, added to this a few drops of litmus solution, and ran into this liquid, from a burette, a solution in water of sulphur trioxide until the colour of the litmus in the solution was just neutral,—if you did these things, it is evident that you would have found the weight of potassium oxide, or potassium hydroxide, which a determinate volume of the solution of sulphur trioxide would react with to form a solution neutral to litmus; in other words, you would have found the *potash-neutralising power* of the solution of sulphur trioxide.

Suppose that 10 grams of caustic potash (potassium hydroxide) were dissolved in 1 litre (1,000 c.c.) of water, and that 50 c.c. of this solution were withdrawn by means of a pipette and placed in a beaker; this 50 c.c. of liquid would contain $\frac{10 \times 50}{1000} = 0.5$ gram of caustic potash. Now, suppose that the mean of two experiments showed that 45.5 c.c. of a certain solution of sulphur trioxide—that is, a solution of sulphuric acid, for sulphuric acid is produced when sulphur trioxide is dissolved in water—were required to neutralise the potash in the 50 c.c. of solution of potash used in the experiment; then, as 45.5 c.c. of the sulphuric acid solution neutralised 0.5 gram of caustic potash, it follows that 1 c.c. of this sulphuric acid solution would neutralise $\frac{0.5}{45.5} = 0.01098$ gram of caustic potash.

If you were given another solution of caustic potash, you would be able to find the weight of potash present in a determinate volume of that solution—that is, to find the *strength* of

that solution of potash—by the use of the *standardised solution of sulphuric acid*. Suppose you measured off 50 c.c. of the solution of potash given you, added a few drops of litmus solution, ran in the standardised solution of sulphuric acid from a burette, until the liquid was neutral (as indicated by the colour of the litmus), and found that 40.2 c.c. of the standardised acid solution were required; then, as 1 c.c. of the standardised acid solution neutralises 0.01098 gram of caustic potash, it follows that 40.2 c.c. must neutralise $0.01098 \times 40.2 = 0.441896$ (say 0.4414) gram of potash; hence, 50 c.c. of the solution of potash given you contain 0.4414 gram of potash; and, therefore, 1 c.c. contains $\frac{0.4414}{50} = 0.008828$ (say 0.00883) gram of potash. This result is expressed by saying that *the strength of the potash solution is 0.00883 gram potash (KOH) per c.c.*

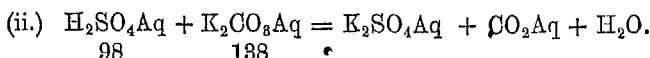
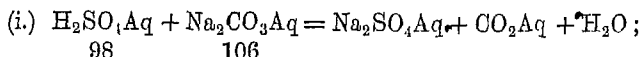
You could also make use of the standardised solution of sulphuric acid to determine the strength of a solution of caustic soda; for you know that 40 grams of soda (NaOH) interact with the same weight of sulphuric acid as 56 grams of potash (KOH). The reaction between a solution of sulphuric acid and a solution of caustic soda, and the reaction between that acid and a solution of caustic potash, are expressed by the equations:—



Now, as the reacting weight—that is, the weight expressed by the formula—of caustic soda is 40 (Na = 23, O = 16, H = 1), and the reacting weight of caustic potash is 56 (K = 39, O = 16, H = 1), these representations in the form of equations of the chemical changes that proceed between a solution of sulphuric acid on the one hand, and a solution of caustic soda and one of caustic potash on the other hand, make patent the fact that 40 parts by weight of caustic soda are *equivalent* to 56 parts by weight of caustic potash as regards the weight of sulphuric acid required to neutralise the soda and the potash respectively. You found that 1 c.c. of the standardised sulphuric acid solution neutralised 0.01098 gram

of caustic potash (KOH) (p. 150); hence 1 c.c. must neutralise $\frac{0.01098 \times 40}{56} = 0.00784$ gram of caustic soda (NaOH).

The reactions that proceed between aqueous solutions of sulphuric acid and sodium carbonate, and aqueous solutions of sulphuric acid and potassium carbonate, are expressed by the following equations:—



$$(\text{Na}=23, \text{K}=39, \text{C}=12, \text{O}=16, \text{S}=32.)$$

If these equations are compared with those which express the reactions between solutions of sulphuric acid and caustic soda, and sulphuric acid and caustic potash (p. 151), it will be seen that 40 parts by weight of caustic soda, 56 parts by weight of caustic potash, 53 parts by weight of sodium carbonate, and 69 parts by weight of potassium carbonate, are equivalent to one another, in that each of these quantities by weight is neutralised by the same weight (namely, 49 parts by weight) of sulphuric acid. Now, if the reaction between a solution of sulphuric acid and one of sodium carbonate, or one of potassium carbonate, takes place fairly rapidly, and if you have some means for finding out accurately when the reaction is completed, it is evident that you can determine the strength of a solution of either of these carbonates (that is, the weight of either carbonate in a determinate volume of the solution) by using the solution of sulphuric acid which you standardised against a solution of caustic potash of known strength. For as 1 c.c. of the standardised sulphuric acid solution neutralised 0.01098 gram of potash (KOH), it follows that 1 c.c. of the same acid solution must neutralise $\frac{0.01098 \times 40}{56}$

$$= 0.00784 \text{ gram of soda (NaOH)}, \text{ and } \frac{0.01098 \times 53}{56} = 0.01039$$

$$\text{gram of sodium carbonate (Na}_2\text{CO}_3), \text{ and } \frac{0.01098 \times 69}{56} = 0.01353$$

$$\text{gram of potassium carbonate (K}_2\text{CO}_3).$$

The foregoing considerations illustrate the principle and the methods of volumetric, or titrimetric, quantitative analysis. The substance to be estimated is caused to interact, when in solution, in a definite and known way with a standardised (or standard) solution of a reagent, and the end of the interaction is determined by some visible change that occurs, either in the reacting substances themselves, or in some other substance used as an indicator. The essentials of a good volumetric method are that the reaction between the standard reagent and the substance to be estimated, which is made the basis of the method, shall be perfectly definite, and shall not be influenced by moderate changes in such conditions as temperature or amount of water present; that the reaction shall proceed rapidly; and that there shall be a sharp and unmistakable indication of the completion of the reaction.

• Those methods of quantitative analysis which are performed with standard solutions of reagents are called *volumetric* methods, because measurements are made of the volumes of the solutions which interact; they are also known as *titrimetric* methods, because standard solutions, that is, solutions of determinate strength, are employed (French, *titre*=standard).

The following explanations of terms that are very often used in volumetric analyses will be useful:—

A standard solution is a solution the strength of which is known.

The strength of a solution is the weight of a stated element or compound in a specified volume of the solution.

The titre of a solution is the same as the strength of the solution.

Titration is the process of determining the quantity of a substance in a solution by running in a standard solution.

Titrating back. When a measured volume of a standard solution, which volume is more than sufficient to accomplish the reaction, is run into a solution that is being analysed, and the excess of the standard solution that has not been changed in the reaction is deter-

mined by means of another standard solution, the latter part of this process is often called *titrating back*.

An *indicator* is a substance which serves to indicate the end of the reaction that is made use of in a titration process.

The terms *normal*, *decinormal*, *pentanormal* . . . *n-normal*, will be understood better when some analyses have been performed with standard solutions.

Special Apparatus used in Volumetric Analyses

Burettes.—A burette is a graduated tube arranged so that a liquid can be allowed to flow from it drop by drop. Burettes are generally graduated from 0 to 50 c.c., and each c.c. is usually divided into tenths (see fig. 84). The lower end is narrowed, and there is a glass stopcock, or a pinch-cock which is fitted on to a rubber joint, near the orifice. A simple and convenient method of closing the burette is to put a little piece of glass rod, rounded at both ends by fusion in a hot flame, inside the caoutchouc tube which joins the burette to a small piece of glass tubing narrowed at its lower end; this piece of glass rod prevents the liquid flowing from the burette. When the caoutchouc tube is pinched to one side the liquid flows between the caoutchouc and the glass rod, and when the hand is removed the flow of liquid ceases. Before a burette is used it should be washed with distilled water, the water being allowed to flow through the burette; the burette should then be rinsed with a little of the

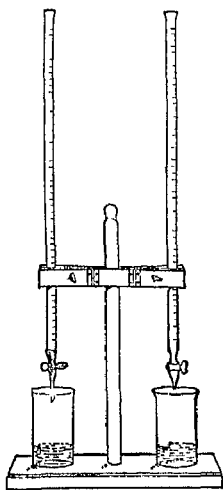


FIG. 84

standard liquid that is to be used, and the liquid should be allowed to flow from the lower end of the burette. The instrument should then be filled to somewhat above the zero mark with the standard liquid, which should be allowed to flow from

the lower end of the burette until the level of the liquid is exactly at the zero mark. When adjusting the level of the liquid, the zero mark must be opposite the eye, and the burette must be filled with the liquid to the tip of the lower end. If the top of the meniscus curve of the surface of the liquid is brought to the zero mark, the level of the liquid left in the burette when the analysis is completed must be read off from the top of the meniscus; and if the bottom of the meniscus is brought to the zero mark, the level must be read off from the bottom of the meniscus at the close of the experiment (see fig. 35). Reading from the bottom of the meniscus is, on the whole, more accurate when the standard solution is colourless; and reading from the top of the meniscus is recommended when the standard solution is deeply coloured. Devices have been invented for helping to read the level of the liquid in a burette accurately; the simplest is to hold a piece of white paper behind the burette near the surface of the liquid.¹ Before running in the standard liquid from a burette see that the instrument is dried outside.

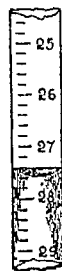


FIG. 35

Pipettes.—A pipette is a fairly wide glass tube fused on to two pieces of narrower glass tubing, as shown in fig. 36. A pipette delivers a determinate volume of liquid, at a definite temperature. This volume is marked on the instrument. Pipettes to deliver 5 c.c., 10 c.c., 25 c.c., and 50 c.c., at the ordinary temperature—say at 15°—are those which are most frequently used in volumetric analyses. The lower end of a pipette is narrowed considerably; the upper end should also be narrowed slightly. Before it is used, a pipette should be washed with distilled water and then rinsed with a little of the solution that is to be analysed. The liquid to be analysed should then be sucked into the pipette till it is above the mark on the stem, when the first finger should be quickly and firmly pressed against the upper end of the instrument. By slightly relaxing the



FIG. 36

¹ Directions for calibrating burettes will be given in the more advanced part of the course.

pressure of the finger the liquid is allowed to flow out of the pipette until the level of the bottom of the meniscus curve is exactly opposite the mark; while this is done the mark on the pipette must be exactly opposite the eye. The measured volume of solution is then allowed to flow from the pipette into the beaker, or other vessel, wherein the estimation is to be conducted; after draining for a moment or two, with the end of the pipette touching the inside of the vessel, a single puff of air is sent by the mouth through the pipette.¹ Pipettes that are graduated to cubic centimetres along the stem are sometimes used for delivering varying volumes of liquid.

Measuring Flasks.—Flasks with long narrow necks, which contain, or deliver, stated volumes of liquid at a definite temperature, are often used in volumetric analyses. The capacity of the flask, to the mark on the neck, and the temperature at which that capacity is determined, are marked on each flask. Flasks which are graduated to 1 litre (1,000 c.c.), $\frac{1}{2}$ litre (500 c.c.), $\frac{1}{4}$ litre (250 c.c.), and 100 c.c., are the sizes used most frequently. Measuring flasks should be fitted with well-ground glass stoppers. If there is only one mark on the neck of a measuring flask, it must be known whether the flask contains, or delivers, the volume of liquid marked on it when it is filled to that mark. If there are two marks on the neck, the flask contains the volume marked on it when it is filled to the lower mark, and delivers the same volume when it is filled to the upper mark and the liquid is poured out and the flask is allowed to drain for a short time, say for ten or fifteen seconds.²

NOTE ON THE USE OF FORMULÆ.—In the following lessons a formula in **heavy type** represents a solid substance; a formula in ordinary type represents a liquid, or if the formula is followed by the symbol Aq an aqueous solution of the substance is to be understood; a formula in *italics* represents a gaseous substance. Formulæ are sometimes employed qualitatively, in place of the names of the substances, for the sake of brevity, and at times

¹ Directions for testing the accuracy of pipettes will be given in the more advanced part of the course.

² Directions for testing the accuracy of measuring flasks will be given in the more advanced part of the course.

for the sake of greater definiteness; but equations which represent chemical changes are always to be read quantitatively.

In this part of the course only a few fairly representative volumetric analyses will be performed. A more extended course of volumetric analysis will be given in the more advanced portion of the work.

In the present part it will be assumed that the student is supplied with the standard solutions that are required.

LESSON XXIX.

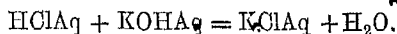
ESTIMATIONS OF THE WEIGHTS OF VARIOUS ACIDS IN SOLUTIONS, GIVEN THE STANDARD SOLUTIONS THAT ARE NECESSARY

Apparatus and materials required.—Standard solution of potash. Standard solution of soda; also unstandardised solution of soda. Standard solution of nitric acid. Solutions of hydrochloric acid, sulphuric acid, and acetic acid, the strengths of which are known but are not indicated on the bottles. Neutral litmus solution (see Note at end of lesson). Methyl orange solution (see Note at end of lesson). Burette graduated in $\frac{1}{10}$ c.c. from 0 to 50 c.c. Pipettes to deliver 10 c.c., 25 c.c., and 50 c.c.

Experiment I.—*To find the grams of hydrochloric acid (HCl) in 1 c.c. of an aqueous solution of that acid; given a standard potash solution.*

NOTE.—In the experiments in this lesson, where the strength of a solution is indicated by the use of the sign of equality, that sign means 'contains'; for instance, '1 c.c. KOHAq = .0056 gram KOH,' means '1 c.c. of the potash solution contains .0056 gram solid potash.'

REACTION.—The reaction which occurs when potash solution is added to HClAq until the solution is exactly neutral is as follows:—



This equation tells that 36.5 grams of hydrochloric acid (HCl) are neutralised by 56 grams of potash (KOH).

If the weight of potash (KOH) required to neutralise an unknown weight of hydrochloric acid (HCl) is known, the

weight of hydrochloric acid neutralised is easily calculated from the equation.

PROCESS.—Measure into a beaker, of about 200 c.c. (say 8 oz.) capacity, a certain volume of the given HClAq ; 25 c.c. is a convenient quantity; add 6 or 8 drops neutral litmus solution, and a little water; place the beaker on white paper, and run in the given *standard potash solution* from a burette, *shaking constantly*, until the litmus assumes the neutral colour. Repeat the titration twice, using in one case 10 c.c., and in the other case 25 c.c., of the HClAq . If the three titrations agree closely, take the mean.

CALCULATION.—Suppose 25 c.c. of the HClAq to be taken; and suppose that 20 c.c. of a standard potash solution of such a strength that 1 c.c. = .0056 gram KOH were used; then the weight, in grams, of KOH used for neutralisation was

$$20 \times .0056 = .112 \text{ gram.}$$

(1 c.c. KOH contains .0056 gram KOH ; therefore 20 c.c. contain $.0056 \times 20$ gram KOH .)

Now, as 56 grams KOH neutralise 36.5 grams HCl (in solution), it follows that .112 gram KOH must neutralise .073 gram HCl :

$$\frac{36.5 \times .112}{56} = .073.$$

Therefore the 25 c.c. HClAq used for the estimation contained .073 gram HCl .

Therefore 1 c.c. of the given HClAq contains .00292 gram HCl .

Perform three other titrations of the hydrochloric acid solution, using methyl orange as indicator.

NOTE.—*Titration in which methyl orange is used as indicator must be conducted with cold liquids.*

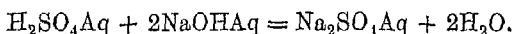
Note on Calculations.—If the student will take care to distinguish clearly figures which represent weights of solid substances from those which represent volumes of solution, he will

have no difficulty in performing the calculations. When a calculation is being worked out, there should be noted opposite the figures obtained at each step of the process exactly what these figures represent. Figures representing volumes (cubic centimetres) must be applied only to solutions. Care must be taken to distinguish between compounds and aqueous solutions of these compounds; for instance, potash is not to be confounded with an aqueous solution of potash. The use of the symbol Aq will be found very convenient; for instance, one might write, with sufficient accuracy, 6 grams, or '005 gram, **KOH**, but not 6 c.c. **KOH**. If it is wished to express shortly, '6 c.c. of an aqueous solution of potash,' it is convenient to write '6 c.c. **KOH**Aq.'

The student must accustom himself to write out his results, and record his calculations, in a clear and methodical way.

Experiment II.—*To find the strength of a solution of sulphuric acid; given a standard solution of caustic soda.*

REACTION.—The reaction which occurs when soda solution is added to sulphuric acid solution until the liquid is exactly neutral is as follows:—



This equation tells that 49 grams of sulphuric acid (H_2SO_4) are neutralised by 40 grams of soda (**NaOH**). [$\text{H}_2\text{SO}_4 = 98$; $2\text{NaOH} = 80$.]

PROCESS.—Measure into a beaker, of about 200 c.c. (say 6 oz.) capacity, 10 c.c. of the given sulphuric acid solution; add 6 or 8 drops neutral litmus solution, and a little water. Place the beaker on white paper, and run in the *standard caustic soda solution* from a burette, *shaking constantly*, until the litmus assumes the neutral tint. Repeat the titration twice, using 25 c.c. of the $\text{H}_2\text{SO}_4\text{Aq}$ each time, and employing methyl orange as an indicator. If the three titrations agree fairly closely, take the mean.

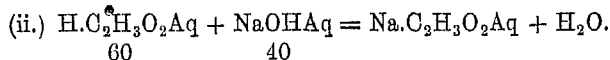
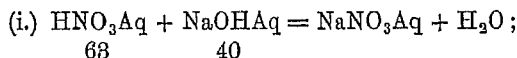
CALCULATION.—Suppose that 50 c.c. of the $\text{H}_2\text{SO}_4\text{Aq}$ required 45.8 c.c. of the standard soda solution for neutralisation; and

suppose that 1 c.c. of the standard soda = 0.0044 gram NaOH ; then the weight of NaOH used was $45.3 \times 0.0044 = 0.19982$ gram. As 40 grams NaOH neutralise 49 grams H_2SO_4 in solution, it follows that 0.19982 gram NaOH must neutralise $\frac{0.19982 \times 49}{40} = 0.24417$ gram H_2SO_4 . Now, as 0.24417 gram H_2SO_4 is contained in 50 c.c. of the H_2SO_4 aq. the strength of which was to be found, it follows that the strength of the given solution of sulphuric acid is expressed by any one of the following statements:—

$$\begin{aligned} 1 \text{ c.c.} &= 0.004888 \text{ gram } \text{H}_2\text{SO}_4 \\ 10 \text{ c.c.} &= 0.04888 \quad \text{,,} \quad \text{,,} \\ 100 \text{ c.c.} &= 0.4888 \quad \text{,,} \quad \text{,,} \\ 1 \text{ litre} &\text{ contains } 4.888 \text{ gram } \text{H}_2\text{SO}_4. \end{aligned}$$

Experiment III.—*To find the strength of a solution of acetic acid; given an unstandardised caustic soda solution, and a standard solution of nitric acid.*

REACTIONS.—The reactions which occur when solutions of nitric acid and acetic acid respectively are neutralised by soda solution are as follows:—



These equations tell that 40 grams of caustic soda (NaOH) neutralise $\left\{ \begin{array}{l} 63 \text{ grams nitric acid (HNO}_3\text{)} \\ 60 \text{ grams acetic acid (H.C}_2\text{H}_3\text{O}_2\text{)} \end{array} \right\}$, or that any definite weight of caustic soda neutralises weights of nitric acid and acetic acid respectively which are in the ratio of 63 to 60.

PROCESS.—I. Measure into a beaker 10 c.c. of the given nitric acid solution, add 6 or 8 drops of a neutral solution of litmus, and a little water; place the beaker on white paper, and run in the unstandardised soda solution from a burette, *shaking*

constantly, until the litmus assumes the neutral tint. Repeat the titration, using 25 c.c. of the HNO_3Aq , and methyl orange as indicator. If the titrations agree fairly closely, take the mean, and enter the result in your note-book in this form : •

25 c.c. standardised HNO_3Aq are neutralised by x c.c. NaOHAq
(putting in the value of x).

II. Repeat the process described in I., but use (i.) 10 c.c., (ii.) 25 c.c., of the given acetic acid solution, and employ *phenolphthaleïn* in both cases as indicator.

Enter the result in your note-book in this form :

25 c.c. $\text{H.C}_2\text{H}_3\text{O}_2\text{Aq}$ are neutralised by y c.c. NaOHAq
(putting in the value of y).

CALCULATIONS.—I. Suppose you found that 25 c.c. HNO_3Aq are neutralised by 20.2 c.c. NaOHAq , and that 25 c.c. $\text{H.C}_2\text{H}_3\text{O}_2\text{Aq}$ are neutralised by 18.5 c.c. of the same NaOHAq ; it follows that $\frac{25 \times 20.2}{18.5} = 27.3$ c.c. of the $\text{H.C}_2\text{H}_3\text{O}_2\text{Aq}$ will be neutralised by 20.2 c.c. of the NaOHAq .

You have then this statement :

{ 25 c.c. HNO_3Aq are neutralised by 20.2 c.c. NaOHAq ;
{ 27.3 c.c. $\text{H.C}_2\text{H}_3\text{O}_2\text{Aq}$ are neutralised by 20.2 c.c. NaOHAq .

II. Now, the HNO_3Aq was a standard solution : suppose 1 c.c. of it contained .0060 gram HNO_3 , then 25 c.c. (the volume used in the analysis) contained $25 \times .006 = .150$ gram HNO_3 . Now you know, from the equations given already, that any specified weight of caustic soda (NaOH) neutralises weights of nitric and acetic acids which are in the ratio of 63 (HNO_3) to 60 ($\text{H.C}_2\text{H}_3\text{O}_2$); as your experiments indicate that the weight of caustic soda which neutralises .150 gram of nitric acid (HNO_3) also neutralises that weight of acetic acid ($\text{H.C}_2\text{H}_3\text{O}_2$) which is contained in 27.3 c.c. of the solution of acetic acid whose strength you are determining, it follows that this weight of acetic acid must be $\frac{60 \times .150}{63} = .14286$ gram.

That is to say, you have found that 27.3 c.c. of the given $\text{H.C}_2\text{H}_3\text{O}_2\text{Aq}$ contains .14286 gram $\text{H.C}_2\text{H}_3\text{O}_2$; hence,

1 c.c. of the given acetic acid solution contains .00523 gram $\text{H.C}_2\text{H}_3\text{O}_2$;

or, 100 c.c. of the given acetic acid solution contain .523 gram $\text{H.C}_2\text{H}_3\text{O}_2$;

or, 1 litre of the given acetic acid solution contains 5.23 grams $\text{H.C}_2\text{H}_3\text{O}_2$.

NOTES ON NEUTRAL LITMUS, METHYL ORANGE, AND PHENOLPHTHALEIN SOLUTIONS AS INDICATORS

Neutral litmus solution is prepared by heating nearly to boiling about 50 grams of powdered litmus (a blue colouring matter obtained from certain lichens) with about half a litre of distilled water, in a basin, for some hours, allowing to settle, decanting the clear liquid, again digesting the residue with hot water for some hours, and again decanting the clear liquid. The mixed liquids are then evaporated to about 500 c.c., a slight excess of acetic acid is added, and the liquid is evaporated till it begins to get thick; about 500 c.c. of warm methylated spirit are then added, whereby the pure blue colouring matter is precipitated; the pp. and liquid are thrown on to a large filter; the solid matter on the filter is washed two or three times with hot methylated spirit, and the washed substance is then dissolved by pouring warm distilled water on to the filter. An exceedingly sensitive solution of litmus may be obtained by boiling 100 grams powdered litmus with 700 c.c. water for some time, decanting the clear liquid, boiling the residue with 300 c.c. water, and decanting; mixing both quantities of liquid, and again decanting after standing for two days. Hydrochloric acid is then added to the liquid till it is very decidedly acid, and the solution is dialysed, in running water, until the liquid in the dialyser is perfectly neutral; this process will occupy about a week. The neutral liquid is then diluted with distilled water. Litmus solution should be kept in open bottles.

Solution of litmus is coloured purple-red by carbon dioxide in solution.

Neutral methyl orange solution is prepared by dissolving 1 gram of methyl orange in a litre of distilled water.

Methyl orange (also called *tropaeolin D*, and *orange III*) is the sodium salt of phenyl-amido-azo-benzene sulphonic acid. A neutral solution of methyl orange is yellowish red without any shade of pink; acids turn the solution rose-pink, and alkalis or alkaline carbonates turn it yellow. A solution of carbon dioxide does not affect the colour of methyl orange. This indicator must always be used in *cold* solutions.

Methyl orange solution does not indicate the close of a neutralisation process, except when tolerably strong acids are used; it cannot be employed with the common organic acids.

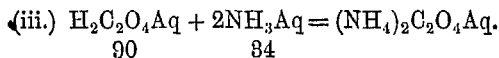
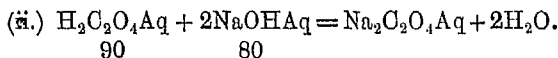
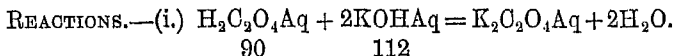
Phenolphthaleïn solution is prepared by dissolving a gram of the compound in about 800 c.c. alcohol (50 per cent.). This solution is colourless in the presence of an acid, but becomes magenta-red with the slightest excess of alkali. Phenolphthaleïn solution is very useful for the titration of weak acids (acetic acid, for instance); such acids do not give sharp colour-changes with litmus or methyl orange.

LESSON XXX

ESTIMATIONS OF THE STRENGTHS OF SOLUTIONS OF ALKALIS AND ALKALINE CARBONATES, GIVEN THE STANDARD SOLUTIONS THAT ARE NECESSARY

Apparatus and materials required.—Standard solution of potash. Standard solution of hydrochloric acid. Unstandardised solution of oxalic acid. Solutions of caustic soda, ammonia, and sodium carbonate, the strengths of which are known but are not indicated on the bottles. Neutral litmus and methyl orange solutions. Burette and pipettes.

Experiment I.—*To analyse quantitatively solutions of caustic soda (NaOH) and ammonia (NH_3); given a standardised solution of potash and an unstandardised solution of oxalic acid.*



These equations tell that any definite weight of oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) when in aqueous solution neutralises weights of potash, soda, and ammonia, respectively, that bear to one another the proportion of 56 (KOH) to 40 (NaOH) to 17 (NH_3).

PROCESS.—I. To 10 c.c. of the given standard potash solution run in the given oxalic acid solution till the liquid is neutral, using litmus as indicator. Repeat the titration with 25 c.c. of the potash solution. Take the mean if the results agree well; if there is a discrepancy of more than .2 c.c., repeat the titration

a third, and if necessary a fourth, time. Enter the result in your note-book thus :

25 c.c. standardised KOHAq = x c.c. of the $\text{H}_2\text{C}_2\text{O}_4\text{Aq}$
(inserting the value of x).

Notice that the sign = here means 'are neutralised by.'

II. Titrate the given soda solution by the oxalic acid solution, making at least two titrations, using *litmus* as indicator. Enter the result thus :

25 c.c. of the NaOHAq = y c.c. of the $\text{H}_2\text{C}_2\text{O}_4\text{Aq}$
(inserting the value of y).

III. Titrate the given ammonia solution by the oxalic acid solution, making at least two titrations, and using *litmus* as indicator. Enter the result thus :

25 c.c. of the NH_3Aq = z c.c. of the $\text{H}_2\text{C}_2\text{O}_4\text{Aq}$
(inserting the value of z).

CALCULATIONS.—I. Calculate the number of c.c. of the soda solution that are neutralised by x c.c. of the oxalic acid solution, that is, by the volume of that acid solution which neutralises 25 c.c. of the standard potash solution; let this volume of the soda solution be a c.c.

II. Calculate the number of c.c. of the ammonia solution that are neutralised by x c.c. of the oxalic acid solution, that is, by the volume of that acid solution which neutralises 25 c.c. of the standard potash solution; let this volume of the ammonia solution be b c.c.

III. You have now obtained these results :

25 c.c. standard KOHAq = x c.c. $\text{H}_2\text{C}_2\text{O}_4\text{Aq}$
 a c.c. given NaOHAq = x c.c. „
 b c.c. „ NH_3Aq = x c.c. „

The weights of **KOH**, **NaOH**, and NH_3 in the three volumes 25 c.c., a c.c., and b c.c., must be in the ratio of 56 : 40 : 17. Now, as the KOHAq is a standard solution, a simple multiplication gives you the grams of **KOH** in 25 c.c. of that solution; knowing this it is easy to find the grams of **NaOH** in a c.c. of the NaOHAq, and the grams of NH_3 in b c.c. of the NH_3Aq .

Divide the grams of NaOH thus found by a , and the grams of NH_3 thus found by b , and you have the grams of NaOH , and the grams of NH_3 , respectively, in 1 c.c. of each solution.

The following example will make the method clear:—

Standard KOHAq 1 c.c. = .0056 gram **KOH**.

25 c.c. standard KOHAq = 25 c.c. $\text{H}_2\text{C}_2\text{O}_4\text{Aq}$.

25 c.c. given NaOHAq = 22.2 c.c. „

25 c.c. „ NH_3Aq = 20.8 c.c. „

Now, $\frac{25 \times 25}{22.2} = 28.15$; and $\frac{25 \times 25}{20.8} = 30.05$;

hence, 25 c.c. standard KOHAq = 25 c.c. $\text{H}_2\text{C}_2\text{O}_4\text{Aq}$;

28.15 c.c. given NaOHAq = 25 c.c. „

30.05 c.c. „ NH_3Aq = 25 c.c. „

Now, 25 c.c. standard KOHAq contain $25 \times .0056$
= .140 gram **KOH**;

hence, 28.15 c.c. of the given NaOHAq contain $\frac{.14 \times 40}{56}$

= .10 gram **NaOH**;

and 30.05 c.c. of the given NH_3Aq contain $\frac{.14 \times 17}{56}$

= .0425 gram NH_3 .

Finally, $\frac{.10}{28.15} = .00355$; and $\frac{.0425}{30.05} = .00144$.

Hence, the results are:—

1 c.c. of the given NaOHAq contains .00355 gram **NaOH**;

and 1 c.c. „ „ NH_3Aq „ .00144 „ NH_3 .

Experiment II.—To find the grams of sodium carbonate in one litre of a solution of that salt; given a standard solution of hydrochloric acid.

REACTION.— $\text{Na}_2\text{CO}_3\text{Aq} + 2\text{HClAq} = 2\text{NaClAq} + \text{CO}_2 + \text{H}_2\text{O}$.

106 78

This equation tells that the weights of hydrochloric acid (HCl) and sodium carbonate (Na_2CO_3) which react, in aqueous solutions, to form a neutral liquid, are in the ratio of 36.5 to

58. Some of the CO_2 which is produced if the reaction escapes as gas, but some remains in solution in the liquid; if the liquid is boiled for some minutes the whole of the carbon dioxide is driven out as gas. Now, CO_2Aq changes the colour of neutral litmus to wine-red; but CO_2Aq does not affect the colour of methyl orange. If, then, litmus is used as indicator the liquid must be boiled, and the close of the reaction must be determined in a boiling liquid; but if methyl orange is used as indicator the titration is performed without heating.

PROCESS.—I. Measure 10 c.c. of the given $\text{Na}_2\text{CO}_3\text{Aq}$ into a beaker, add a little water, and a few drops of neutral litmus solution. Run in the standard acid solution until a reddish purple colour is produced in the liquid, and then boil for a few minutes. The colour of the solution will go blue, showing that all the Na_2CO_3 in solution has not been neutralised. Now keep the solution boiling, and *very slowly* run in the standard acid solution *drop by drop, taking care that the solution actually boils for a few moments after each small addition of acid*, until the neutral colour is produced. Repeat the titration, using 25 c.c. of the $\text{Na}_2\text{CO}_3\text{Aq}$.

II. Measure 10 c.c. of the given $\text{Na}_2\text{CO}_3\text{Aq}$ into a beaker, add a little water, and a few drops of neutral methyl orange, and run in the standard acid solution, *without warming*, until the neutral colour appears. Repeat the titration, using 25 c.c. of the $\text{Na}_2\text{CO}_3\text{Aq}$.

CALCULATION.—Suppose the standard HClAq were of such a strength that

$$1 \text{ c.c.} = 0.00865 \text{ gram HCl};$$

and suppose that 25 c.c. of the $\text{Na}_2\text{CO}_3\text{Aq}$ were neutralised by 26.8 c.c. of the standard HClAq . Then, grams of HCl used = $26.8 \times 0.00865 = 0.09782$.

Hence, from equation which expresses the reaction, grams of Na_2CO_3 neutralised by 0.09782 gram $\text{HCl} = \frac{53 \times 0.09782}{36.5} = 1.420$. Now, as 25 c.c. of the $\text{Na}_2\text{CO}_3\text{Aq}$ were used, there is 1.42 gram Na_2CO_3 in this 25 c.c., which is equal to 5.68 gram in 100 c.c.

Hence, one litre of the solution of sodium carbonate contains 5.68 grams of the salt Na_2CO_3 .

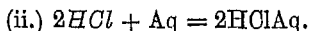
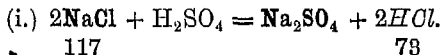
LESSON XXXI

PREPARATION OF SOLUTIONS OF HYDROCHLORIC ACID, AND AMMONIA, OF SPECIFIED STRENGTHS; THE STANDARD SOLUTIONS THAT ARE REQUIRED BEING GIVEN

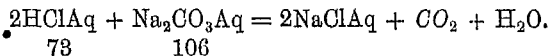
Apparatus and materials required.—Standard solution of sodium carbonate. Standard solution of sulphuric acid. Sodium chloride. Ammonium chloride. Caustic soda. Litmus and methyl orange solutions. Flask of about 8 or 10 oz. capacity, fitted with caoutchouc cork carrying a funnel-tube and an exit-tube bent twice at right angles, the longer limb being about 400 mm. (15 inches) long.

Experiment I.—*Preparation of a solution of hydrochloric acid containing .005 gram HCl per c.c.; given sodium chloride and conc. sulphuric acid, and a standardised solution of sodium carbonate.*

REACTIONS.—I. For the preparation of a solution of hydrochloric acid.



II. For titration of the solution of hydrochloric acid.



Reaction (i.) shows that 73 grams of HCl are obtained by the complete decomposition of 117 grams of $NaCl$; suppose it is decided to prepare about a quarter litre (250 c.c.) of the solution of hydrochloric acid containing .005 gram HCl per c.c., the weight of HCl that should be present in this 250 c.c. of water will be $.005 \times 250 = 1.25$ grams; to give this weight of HCl ,

$\frac{117 \times 1.25}{78} = 2.00$ grams of common salt will be required.

More than this weight of salt should be used, as it is not likely that the whole of the salt will be decomposed; and, moreover, matters should be arranged so that the solution of hydrochloric acid is certain to be stronger than is directed, because it is very easy to dilute a solution to a specified strength, but if a solution is not strong enough the process of preparing the substance in the solution must be performed a second time.

PROCESS.—I. Set up an apparatus like that described in Lesson XXIV., *Experiment I* (fig. 28, p. 114); put about 250 c.c. of distilled water in the beaker, and about 6 to 8 grams of sodium chloride (about half a test-tubeful) in the flask; and proceed as directed on p. 114 until the evolution of gas has nearly ceased.

II. *Thoroughly mix* the solution of hydrochloric acid you have prepared by *repeatedly shaking the beaker*. Withdraw 10 c.c. of the liquid, and determine its strength by titration with the standardised $\text{Na}_2\text{CO}_3\text{Aq}$, using methyl orange as indicator; repeat the titration with (i.) 10 c.c., (ii.) 25 c.c. Take the mean of the three titrations, calculate the strength of the solution, and enter the result in your note-book in this form:

1 c.c. HClAq contains x gram HCl (filling in the value of x).

Now calculate the volume of water which must be added to 1 c.c. of the HClAq you have made in order that the liquid thus produced shall contain .005 gram HCl per c.c. (*see forward*); dilute a convenient quantity of the HClAq (say about 25 c.c.) with *exactly* the calculated volume of water (measured from a burette, or from pipettes and a burette), *mix thoroughly*, and make two determinations of the strength of this solution by titration with the standard $\text{Na}_2\text{CO}_3\text{Aq}$, using methyl orange as indicator, to make sure that the solution is exactly of the proper strength.

CALCULATION FOR DILUTION.—Suppose you found that 1 c.c. of the HClAq you made contains .01455 gram HCl . You must increase the bulk of 1 c.c. of this solution by adding such a

volume of water that 1 c.c. of the new solution shall contain $\cdot 005$ gram HCl ; in other words, you must cause the $\cdot 01455$ gram of HCl , now present in 1 c.c. of the solution, to be disseminated through so much water that when 1 c.c. is taken out of this solution that 1 c.c. contains $\cdot 005$ gram HCl .

Put it in this form: as 1 c.c. of the solution at present contains $\cdot 01455$ gram HCl , what fraction of a c.c. contains $\cdot 005$ gram HCl ? Evidently $\frac{\cdot 005 \times 1}{\cdot 01455} = \cdot 3436$ c.c. If, then, you measured off $\cdot 3436$ c.c. of the solution, and added to this $\cdot 6564$ c.c. water ($1 - \cdot 3436 = \cdot 6564$), you would have 1 c.c. of a solution containing $\cdot 005$ gram HCl . You cannot measure off $\cdot 3436$ c.c. of the solution; but you can measure off $34\cdot 4$ c.c., and add to this $65\cdot 6$ c.c. of water, and so obtain 100 c.c. of a solution of the desired strength.

Or, put it in this form: if 1 c.c. of the solution contained 1 milligram of HCl , and it was desired that 1 c.c. should contain half a milligram of HCl , it is evident that you would have to double the volume of the solution by adding water (for then the solution would contain 1 mgm. HCl in 2 c.c., and, therefore, half a mgm. in 1 c.c.); hence, if you increase the volume of 1 c.c. of the solution you have made in the ratio of $\cdot 005$ to $\cdot 01455$ you will have a solution of the desired strength. Now, $\frac{\cdot 01455}{\cdot 005} = 2\cdot 91$; therefore, to 1 c.c. of the solution you must add 1\cdot 91 c.c. of water, or to 10 c.c. you must add 19\cdot 1 c.c. of water, or to 50 c.c. you must add 95\cdot 5 c.c. of water.

The results of these two ways of considering the matter may be expressed, shortly, as follows:

(i.) Let there be a grams of the compound in 1 c.c.; and let it be desired to have b grams of the compound in 1 c.c. ($b < a$).

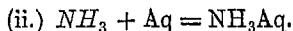
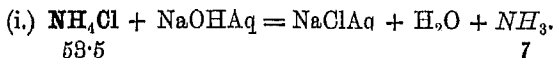
Then $\frac{b}{a} = x$ c.c.; and $1 - x =$ c.c. of water to be added to x c.c. of solution.

(ii.) Let a and b have the same meanings as in (i.).

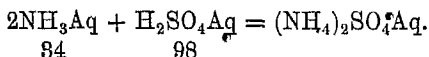
Then $\frac{a}{b} = y$ c.c., and $y - 1 =$ c.c. of water to be added to 1 c.c. of solution.

Experiment II.—*Preparation of a solution of ammonia containing .0015 gram NH_3 per c.c.; given ammonium chloride and caustic soda, and a standard solution of sulphuric acid.*

REACTIONS.—I. For the preparation of a solution of ammonia.



II. For the titration of the solution of ammonia.



Equation (i.) shows that 17 grams of NH_3 are obtained by the complete decomposition of 58.5 grams of NH_4Cl ; that is, whatever weight of NH_3 is required, *about* three times that weight of NH_4Cl must be used. You are asked to prepare about a quarter litre of the solution of ammonia with .0015 gram NH_3 per c.c.

PROCESS.—I. Wash out the apparatus used in *Experiment I.* for making HCl_{Aq} ; put about 4 grams of NH_4Cl (about quarter a test-tubeful) into the flask ($.0015 \times 250 = .375$ gram NH_3 are required; $.375 \times 3$, say, 1.2 grams NH_4Cl , *approximately*, required; about 3 times as much as this should be used), and then add a few test-tubesful of water, and a stick of caustic soda; put about 250 c.c. of distilled water into the beaker, and surround the beaker with cold water; heat the contents of the flask to boiling, and boil for, say, 10 minutes.

II. *Thoroughly mix* the liquid in the beaker; then determine the strength of the solution by titration with the standard sulphuric acid, making three titrations, and using both litmus and methyl orange as indicators. Now calculate the grams of NH_3 in 1 c.c. of the solution. Then calculate the dilution needed to make the solution of the required strength; dilute about 40 or 50 c.c. with the proper volume of water; *mix thoroughly*, and determine, by titration with the standard sulphuric acid, whether the diluted solution is of the proper strength.

LESSON XXXII

EXERCISES ON THE ESTIMATION OF ACIDS, ALKALIS, AND
ALKALINE CARBONATES

THE common alkalis are soda (NaOH), potash (KOH), and ammonia solution (NH_4OH aq, or NH_3 aq); solutions of lime (CaO) and baryta (BaO) are also often classed as alkali solutions.

The commonest acids are hydrochloric (HCl), nitric (HNO_3), sulphuric (H_2SO_4), and acetic ($\text{H.C}_2\text{H}_3\text{O}_2$). Other tolerably common acids in the laboratory are oxalic ($\text{H}_2\text{C}_2\text{O}_4$); and solution of hydriodic acid (HIAq), and hydrobromic acid (HBrAq).

The common alkali carbonates are sodium carbonate (Na_2CO_3), potassium carbonate (K_2CO_3), and ammonium carbonate ($(\text{NH}_4)_2\text{CO}_3$).

If a solution is given to be analysed qualitatively and quantitatively, that solution containing an acid, an alkali, or an alkali carbonate, begin by testing the reaction of it to pieces of red and blue litmus paper. If alkaline, test another portion by adding a little dilute acid and noticing whether there is effervescence or not; as the solutions used in volumetric analysis are necessarily very dilute, the amount of effervescence will be very small. Having thus determined to which of the three classes the compound in solution belongs, apply special tests to determine what the compound is.

Solutions of caustic soda or sodium carbonate impart a deep yellow colour to a hot non-luminous flame, when a clean platinum wire is dipped repeatedly into the solution and is then brought into the flame.

Solutions of caustic potash or potassium carbonate impart a lavender-violet colour (which appear reddish violet through blue glass) to a hot non-luminous flame, when a clean platinum wire is dipped repeatedly into the solution and is then brought into the flame.

A solution of ammonia smells of ammonia, especially when warmed; a piece of red litmus paper turns blue when held in the steam coming off from the warmed liquid.

A solution of ammonium carbonate gives off ammonia when boiled after addition of caustic potash, or soda, solution.

A solution of lime soon becomes turbid on exposure to the air, from formation of CaCO_3 ; the solution gives a white pp. (CaC_2O_4) on addition of ammonium oxalate solution, and the pp. is not dissolved by acetic acid.

A solution of baryta rapidly becomes turbid on exposure to the air, from formation of BaCO_3 , the solution gives a white pp. (BaSO_4) on addition of a little very dilute sulphuric acid; this pp. does not dissolve in hydrochloric acid solution.

A solution of hydrochloric acid gives a white pp. (AgCl) on addition of silver nitrate solution; this pp. is easily soluble in ammonia solution.

A solution of hydrobromic acid gives a nearly white pp. (AgBr) on addition of silver nitrate solution; this pp. is dissolved fairly easily by ammonia. If a solution of hydrobromic acid is mixed with an aqueous solution of chlorine (till the smell of chlorine is apparent), and is then shaken with a few drops of carbon disulphide and allowed to settle, the carbon disulphide separates from the rest of the liquid at the bottom of the test-tube, and is coloured red-brown from the presence of bromine dissolved in it.

A solution of hydriodic acid gives a pale yellow pp. (AgI) with silver nitrate solution; this pp. is nearly insoluble in ammonia. If a solution of hydriodic acid is treated with chlorine water, and then with carbon disulphide, as directed in the test for HBrAq , the carbon disulphide becomes coloured violet-red from the presence of iodine dissolved in it.

A solution of sulphuric acid gives an immediate white pp. (BaSO_4) with solution of barium nitrate, and the pp. is insoluble in HClAq .

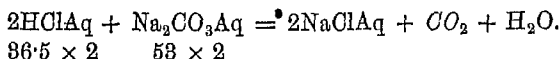
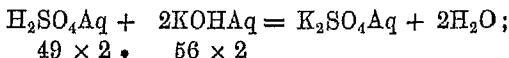
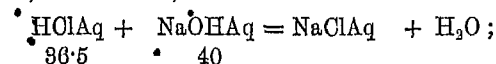
A solution of nitric acid gives a brownish black colour (due to formation of compounds of nitric oxide with ferrous sulphate) when the liquid is mixed with a good deal of conc. sulphuric acid, and cooled thoroughly, and a solution of ferrous sulphate, freshly prepared in cold water, is then slowly poured down the test-tube so as to float on the surface of the heavier liquid containing sulphuric acid. (For detailed directions, see p. 70.)

A solution of oxalic acid gives a white pp. (CaC_2O_4) with solution of calcium chloride, and the pp. is insoluble in acetic acid.

A solution of acetic acid smells of vinegar, especially when warmed. If a solution of acetic acid is mixed with a little ferric chloride solution, and a very dilute solution of ammonia is then added, drop by drop (mixing thoroughly after the addition of each drop), a red colour (due to the formation of ferric acetate) is produced in the liquid before the formation of a reddish pp. (FeO_3H_3) occurs.

NOTE ON NORMAL AND DECINORMAL STANDARD SOLUTIONS OF ACIDS, ALKALIS, AND ALKALINE CARBONATES

The standard reaction is neutralisation of soda or potash by an acid ; for instance,



A solution of that number of grams of an acid which neutralises 40 grams soda or 56 grams potash ($\text{NaOH} = 40$, $\text{KOH} = 56$) in 1 litre (1,000 c.c.) of water is a normal solution of an acid. Thus ($\text{HCl} = 36\cdot5$, $\text{H}_2\text{SO}_4 = 98$) 36·5 grams HCl , or 49 grams H_2SO_4 , in 1 litre of water is a normal solution.

A solution of that number of grams of an alkali, or alkaline carbonate, which neutralises 36·5 grams HCl , or 49 grams H_2SO_4 , in 1 litre of water is a normal solution of an alkali, or alkaline carbonate. Thus ($\text{KOH} = 56$, $\text{Na}_2\text{CO}_3 = 106$) 56 grams KOH , or 53 grams Na_2CO_3 , in 1 litre of water is a normal solution.

Normal solutions are usually denoted by N, and decinormal by $\frac{\text{N}}{10}$; thus $\frac{\text{N}}{10}$ sulphuric acid means a solution containing 4·9 grams of H_2SO_4 per litre = 0·0049 gram H_2SO_4 per c.c.

A specified volume of a normal (or decinormal) solution of any acid is equal in neutralising power to the same volume of a normal (or decinormal) solution of any other acid ; also 1 c.c. N soda solution neutralises 1 c.c. $\frac{\text{N}}{10}$ acid ; 1 c.c. $\frac{\text{N}}{10}$ sodium carbonate solution neutralises 1 c.c. $\frac{\text{N}}{10}$ acid, and so on.

The strengths of decinormal solutions of the commonly used acids, alkalis, and alkaline carbonates, are as follows :—

$\frac{\text{N}}{10}$ HClAq contains 0·00865 gram HCl per c.c. ($\text{HCl} = 36\cdot5$)

$\frac{N}{10}$ HNO_3Aq contains $\cdot 0063$ gram HNO_3 per c.c. ($\text{HNO}_3 = 63$.)

$\frac{N}{10}$ $\text{H}_2\text{SO}_4\text{Aq}$ contains $\cdot 0049$ gram H_2SO_4 per c.c. ($\text{H}_2\text{SO}_4 = 98$.)

$\frac{N}{10}$ $\text{H.C}_2\text{H}_3\text{O}_2\text{Aq}$ contains $\cdot 0060$ gram $\text{H.C}_2\text{H}_3\text{O}_2$ per c.c.
($\text{H.C}_2\text{H}_3\text{O}_2 = 60$.)

$\frac{N}{10}$ $\text{H}_2\text{C}_2\text{O}_4\text{Aq}$ contains $\cdot 0045$ gram $\text{H}_2\text{C}_2\text{O}_4$ per c.c.
($\text{H}_2\text{C}_2\text{O}_4 = 90$.)

$\frac{N}{10}$ NaOHAq contains $\cdot 0040$ gram NaOH per c.c. ($\text{NaOH} = 40$.)

$\frac{N}{10}$ KOHAg contains $\cdot 0056$ gram KOH per c.c. ($\text{KOH} = 56$.)

$\frac{N}{10}$ NH_3Aq contains $\cdot 0017$ gram NH_3 per c.c. = $\cdot 0085$ gram
 NH_4OH per c.c. ($\text{NH}_3 = 17$; $\text{NH}_4\text{OH} = 35$.)

$\frac{N}{10}$ CaOAq contains $\cdot 0028$ gram CaO per c.c. = $\cdot 0037$ gram
 CaO_2H_2 per c.c. ($\text{CaO} = 56$; $\text{CaO}_2\text{H}_2 = 74$.)

$\frac{N}{10}$ BaOAq contains $\cdot 00765$ gram BaO per c.c. = $\cdot 00855$ gram
 BaO_2H_2 per c.c. ($\text{BaO} = 153$; $\text{BaO}_2\text{H}_2 = 171$.)

$\frac{N}{10}$ $\text{Na}_2\text{CO}_3\text{Aq}$ contains $\cdot 0053$ gram Na_2CO_3 per c.c.
($\text{Na}_2\text{CO}_3 = 106$.)

$\frac{N}{10}$ $\text{K}_2\text{CO}_3\text{Aq}$ contains $\cdot 0069$ gram K_2CO_3 per c.c. ($\text{K}_2\text{CO}_3 = 138$.)

$\frac{N}{10}$ $(\text{NH}_4)_2\text{CO}_3\text{Aq}$ contains $\cdot 0048$ gram $(\text{NH}_4)_2\text{CO}_3$ per c.c.
($(\text{NH}_4)_2\text{CO}_3 = 96$.)

THE FOLLOWING EXERCISES ARE GIVEN AS SUGGESTIONS:—

Exercise I.—Analyse qualitatively and quantitatively the solutions A, B, and C; each of which contains an acid, an alkali, or an alkaline carbonate.

Exercise II.—(i.) *What is the strength of the solution D after it has been diluted with its own volume of water?*

(ii.) *If all the oxygen in the acid, alkali, or alkaline carbonate in solution E were obtained, how many c.c. of oxygen, measured at 0° and 760 mm., would be got from 100 c.c. of E?*

Exercise III.—(i.) *If an excess of silver nitrate solution were added to 100 c.c. of solution F, how many grams of silver chloride would be precipitated?*

(ii.) *Each solution, G and H, contains an acid; find how many c.c. of solution H are equivalent in neutralising power to 100 c.c. of solution G.*

Exercise IV.—*Solution K contains an acid, and solution L an alkaline carbonate; from these solutions prepare decinormal solutions of the acid and the alkaline carbonate respectively.*

Exercise V.—(i.) *The solution M contains one-fourth of a gram-molecular weight of a certain acid per litre; find the basicity of the acid. One gram-molecular weight = quantity expressed by molecular weight taken in grams.*

(ii.) *From the ammonium chloride given you prepare about a quarter litre of a decinormal solution of ammonia (NH_3).*

• The following are the quantities by weight (in round numbers) expressed by the formulæ of the commoner alkalis, alkaline carbonates, and acids:—

$NaOH = 40$, $KOH = 56$, $(NH_4)OH = 35$, $NH_3 = 17$; $Na_2CO_3 = 106$, $K_2CO_3 = 138$, $(NH_4)_2CO_3 = 96$; $H_2SO_4 = 98$, $HNO_3 = 63$, $HCl = 36.5$, $H_2C_2O_4 = 90$, $H.C_2H_3O_2 = 60$.

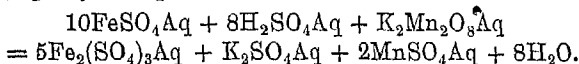
LESSON XXXIII.

ESTIMATION OF THE WEIGHT OF IRON CONTAINED IN A SOLUTION OF A FERROUS COMPOUND, GIVEN THE STANDARD SOLUTIONS THAT ARE NECESSARY

Apparatus and materials required.—Standard solutions of potassium permanganate and potassium bichromate. Solution of ferrous sulphate, the strength of which is known but is not stated on the bottle. Pure potassium ferricyanide. White plate. Burettes and pipettes.

Experiment I.—*To find the grams of iron in an aqueous solution of ferrous sulphate, using potassium permanganate as the standard solution.*

REACTION.—When $K_2Mn_2O_8Aq$ is run into a solution of a ferrous salt in dilute H_2SO_4Aq , a ferric salt is formed, and also sulphates of potassium and manganese. The reaction with $FeSO_4Aq$ may be expressed thus:



[The reaction may be supposed to occur in two stages, taking place at the same time:—

- (1) $K_2Mn_2O_8Aq + 3H_2SO_4Aq$
 $= K_2SO_4Aq + 2MnSO_4Aq + 3H_2O + 5O;$
- (2) $10FeSO_4 + 5H_2SO_4Aq + 5O = 5Fe_2(SO_4)_3Aq + 5H_2O.]$

The equation tells that 316 parts by weight of potassium permanganate in solution ($K_2Mn_2O_8 = 316$) convert 560 parts by weight of iron ($Fe = 56$) in a ferrous salt dissolved in dilute sulphuric acid into the same weight of iron in a ferric salt. It is customary to say that potassium permanganate solution, in presence of sulphuric acid, oxidises ferrous iron to ferric iron.

Hence, 3.16 gram $\text{K}_2\text{Mn}_2\text{O}_8$, in solution, oxidise 5.6 grams ferrous iron to ferric iron. Now, if 3.16 grams $\text{K}_2\text{Mn}_2\text{O}_8$ were dissolved in one litre of water, 1 c.c. of this solution would oxidise .0056 gram iron (from ferrous to ferric iron). The strength of a standard permanganate solution is generally stated in two ways; thus, for a solution of the above strength,

$$1 \text{ c.c.} = .00316 \text{ gram } \text{K}_2\text{Mn}_2\text{O}_8,$$

or

$$1 \text{ c.c.} = .0056 \text{ gram iron.}$$

Notice that the sign of equality has not the same meaning in both statements.

Solutions of the products of the oxidation of a dilute solution of a ferrous salt, in dilute $\text{H}_2\text{SO}_4\text{aq}$, by permanganate, are colourless; permanganate solution itself is deeply coloured. When the oxidising action is finished the next drop of permanganate solution colours the liquid; hence, permanganate solution is its own indicator.

PROCESS.—To 10 c.c. of the given solution of a ferrous salt, in a beaker placed on white paper, add a good deal (say a test-tubeful) of dilute $\text{H}_2\text{SO}_4\text{aq}$, and run in the given standard permanganate solution, *with constant shaking*, until the liquid acquires a very faint pink colour. Repeat this titration twice, using 25 c.c. of the ferrous salt solution.

CALCULATION.—Suppose 25 c.c. of a solution of ferrous sulphate were used, and 20.5 c.c. of a standard permanganate solution were required to effect the oxidation to ferric sulphate; and suppose that

$$1 \text{ c.c. permanganate} = .0038 \text{ gram } \text{K}_2\text{Mn}_2\text{O}_8.$$

As .00316 gram $\text{K}_2\text{Mn}_2\text{O}_8$ oxidises .0056 gram iron, it follows that 1 c.c. of the standard permanganate solution that was used = .0067 gram iron (that is, oxidises .0067 gram iron in a ferrous salt to the same weight of iron in a ferric salt)—

$$\left(\frac{.0056 \times .0038}{.00316} = .0067 \right).$$

Hence, there was $20.5 \times .0067 = .13735$ gram iron in 25 c.c.

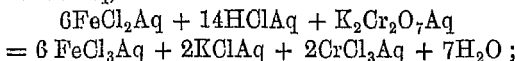
of the solution of the ferrous salt used ; that is, .13735 gram iron is contained, as a ferrous salt, in 25 c.c. of the solution used.

Hence, 1 c.c. of the solution contains $\frac{.13735}{25} = .00549$ gram iron.

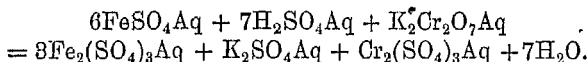
Titrations with permanganate should always be performed in solutions containing sulphuric acid.

Experiment II.—To find the grams of iron in an aqueous solution of ferrous sulphate, using potassium bichromate as the standard solution.

REACTION.— $K_2Cr_2O_7Aq$, in presence of acid and an oxidisable substance, acts as an oxidiser ; thus, with a solution of ferrous chloride in $HClAq$,



or with a solution of ferrous sulphate in H_2SO_4Aq ,



$K_2Cr_2O_7 = 294$. Therefore, 294 grams $K_2Cr_2O_7$, in solution oxidise $6 \times 56 = 336$ grams iron from ferrous to ferric iron ; or $49 \left(= \frac{294}{6} \right)$ grams $K_2Cr_2O_7$ oxidise 56 grams iron.

Therefore, if 4.9 grams $K_2Cr_2O_7$ are dissolved in one litre of water, 1 c.c. of this solution will contain .0049 gram $K_2Cr_2O_7$, and will oxidise .0056 gram iron from ferrous to ferric iron.

When $K_2Cr_2O_7Aq$ is used to oxidise a ferrous salt in solution no marked change of colour occurs ; therefore an indicator must be provided. Ferrous salts in solution give a blue colour (or pp.) with a solution of potassium ferricyanide (K_3FeCy_6Aq) ; ferric salts in solution give scarcely any colour change with the same reagent. These reactions are used to indicate when the oxidation by $K_2Cr_2O_7Aq$ is completed. The indicator (K_3FeCy_6Aq) cannot be added to the ferrous salt solution, because a portion of the iron would be pptd. as Prussian blue and Turnbull's blue.

PROCESS.—To 10 c.c. of the ferrous salt solution, in a beaker

placed on white paper, add a good deal of HClAq (say a test-tubeful); prepare a *very dilute* solution of K_3FeCy_6 (this solution cannot be kept, as it undergoes change), and place several small drops of this solution on a white plate, a *little distance apart from one another*. Now run in the standard $\text{K}_2\text{Cr}_2\text{O}_7\text{Aq}$, with constant shaking, and from time to time remove a *small drop* of the liquid on a glass rod, and let it fall on to one of the drops of $\text{K}_3\text{FeCy}_6\text{Aq}$. *Wash the rod each time*. Proceed thus until a drop of the liquid just ceases to produce any shade of blue, or green-blue, colour in the $\text{K}_3\text{FeCy}_6\text{Aq}$. Repeat the titration twice, using 25 c.c. of the solution of the ferrous salt.

CALCULATIONS.—I. Suppose the standard solution was of such a strength that 1 c.c. = .0045 gram iron; and suppose 20 c.c. had been used to oxidise the iron in 25 c.c. of the given ferrous sulphate solution.

Then $\frac{20 \times .0045}{25} = .0036$ gram iron is contained in each c.c. of the solution analysed.

II. Suppose that the strength of the standard solution used was given in this form:—

$$1 \text{ c.c.} = .0055 \text{ gram } \text{K}_2\text{Cr}_2\text{O}_7.$$

(Notice that the sign of equality here means ‘contains.’) And suppose that 14.6 c.c. of this solution were required to oxidise the iron in 25 c.c. of the ferrous sulphate solution. Then, as 49 grams $\text{K}_2\text{Cr}_2\text{O}_7 = 56$ grams iron, it follows that .0055 gram $\text{K}_2\text{Cr}_2\text{O}_7 = \frac{.56 \times .0055}{49} = .00628$ gram iron.

(Notice that the sign of equality here means ‘oxidises from a ferrous to a ferric compound.’) Hence, $14.6 \times .00628 = .09169$ gram iron was contained in 25 c.c. of the ferrous sulphate solution analysed; and, therefore,

$$1 \text{ c.c. of the solution contains } \frac{.09169}{25} = .00367 \text{ gram iron.}$$

It is advisable to enter the results of the estimations of iron in your note-book in a systematic form. The following arrangement is clear:—

Strength of standard solution: 1 c.c. = $\left\{ \begin{array}{l} \text{gram } \text{K}_2\text{Mn}_2\text{O}_8. \\ \text{gram } \text{K}_2\text{Cr}_2\text{O}_7. \end{array} \right.$

I.

— c.c. of ferrous solution taken.

II.

— c.c. of $\left\{ \begin{array}{l} \text{permanganate solution} \\ \text{bichromate solution} \end{array} \right\}$ used.

III.

Grams of $\left\{ \begin{array}{l} \text{K}_2\text{Mn}_2\text{O}_8 \\ \text{K}_2\text{Cr}_2\text{O}_7 \end{array} \right\}$ used.

IV.

Grams of iron corresponding to
• grams of $\text{K}_2\text{Mn}_2\text{O}_8$, or grams
of $\text{K}_2\text{Cr}_2\text{O}_7$, used.

V.

Grams of iron in 1 c.c. of solution analysed;

$$= \frac{\text{grams in col. IV.}}{\text{c.c. in col. I.}}$$

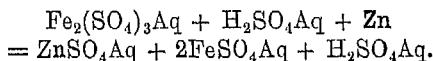
LESSON XXXIV

ESTIMATION OF THE WEIGHT OF IRON CONTAINED IN A SOLUTION OF A FERRIC COMPOUND, GIVEN THE STANDARD SOLUTIONS THAT ARE REQUIRED

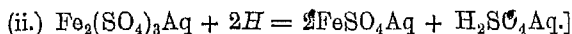
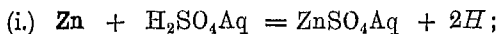
Apparatus and materials required.—Standard solutions of permanganate and bichromate. Solution of ferric chloride in water, the strength of which is known but is not stated on the bottle. Solution of ferric sulphate in dilute sulphuric acid, the strength of which is known but is not stated on the bottle. Granulated zinc, free from iron. Zinc dust, free from iron. Solutions of stannous chloride and mercuric chloride. Pure potassium ferricyanide. White plate. Flask of about 200 c.c. (say 6 oz.) capacity, with good caoutchouc cork carrying a piece of glass tubing about 450 mm. (18 inches) long, drawn to narrow opening at the upper end. Dry reversed filter.

Experiment I.—*To find the grams of iron in a solution of a ferric salt which also contains sulphuric acid, using potassium permanganate as the standard solution.*

REACTION.—Before the iron in a ferric salt solution can be estimated volumetrically, the ferric must be reduced to a ferrous salt; when this has been done the ferrous iron is oxidised to ferric iron by standard permanganate, as in *Experiment I., Lesson XXXIII*. If the solution of the ferric salt contains a fair amount of sulphuric acid, the method of procedure usually adopted is to effect the reduction by dissolving zinc in the solution, whereby the hydrogen that is produced brings about the conversion of the ferric into ferrous sulphate. The following equation may be used to express the chemical change:—



[The reaction may be supposed to occur in two stages occurring simultaneously :—



NOTE.—If the ferric solution contains no acid, or very little acid, it is much more convenient to reduce by zinc dust, as directed in *Experiment II*. If the ferric solution contains hydrochloric acid, the most suitable reducing agent is stannous chloride solution; in this case the titration is performed with standardised bichromate solution, as directed in *Experiment III*.

PROCESS.—The reduction must be effected in such a way that there is no chance of atmospheric oxygen re-oxidising the reduced ferrous salt. A very convenient method of doing this is to warm the acidulated ferric solution with zinc in a flask, closed by a good cork through which passes a piece of rather narrow glass tubing, about 18 inches long, drawn to a fine opening at its upper end. As the hydrogen is thus evolved under a pressure a little greater than that of the atmosphere there is no chance of air entering the apparatus while the solution of the zinc is proceeding. Place 25 c.c. of the ferric solution in a flask of about 6 oz. capacity, fitted with a caoutchouc cork and glass tube as described; add some water and a little diluted sulphuric acid, and then *two or three* (not more) *thin pieces* of zinc, *free from iron*; insert the cork firmly, place the flask on wire gauze on a tripod, and support the glass tube by a clamp. Keep a *small flame* under the flask until a brisk evolution of gas begins, then remove the flame, and allow the action to proceed until the zinc is completely dissolved; a few pieces of lead (a common impurity in zinc) may remain, but *the evolution of gas must have ceased entirely in the warm liquid before proceeding with the titration*.

NOTE.—It will save time to proceed with *Experiment II*, while the reduction of the ferric solution is being effected.

If the action slackens much place a *low flame* under the flask for a little time, but take care that the evolution of gas does not become very rapid, else the cork may be blown out of the flask.

If the liquid in the flask is not *quite colourless* when the zinc has dissolved, some ferric salt is still present; in this case take out the cork, *quickly* drop in *one or two thin pieces* of zinc, *at once* insert the cork, and proceed as directed already.

When the solution is quite colourless and the whole of the zinc has dissolved, let the liquid cool; then remove the cork, take out a *small* drop of the liquid on the end of a clean glass rod, and *at once* let it fall on to a drop of potassium sulphocyanide solution on a piece of filter paper; if no colour, or at most an extremely faint pink colour, is produced where the two liquids meet, the whole of the ferric has been reduced to a ferrous salt. If, however, the potassium sulphocyanide solution produces a red colour with the drop of liquid taken from the flask, some ferric salt is still present; in this case you must add one or two *very small pieces* of zinc, and a little diluted sulphuric acid, to the contents of the flask, and proceed as directed before, until the whole of the zinc is dissolved and one drop of the cold liquid taken from the flask gives no colour, or at most an extremely faint pink colour, with a drop of potassium sulphocyanide solution.

(KONSAq reacts with a ferric salt in solution to produce $\text{Fe}(\text{CNS})_3\text{Aq}$, which is deep red.)

When the reduction is completed and the zinc has dissolved, remove the cork from the flask, add a test-tubeful of diluted sulphuric acid (to make sure there is sufficient $\text{H}_2\text{SO}_4\text{Aq}$ to react with the permanganate), and at once run in standard potassium permanganate solution until a faint pink colour is produced in the liquid.

CALCULATION.—Proceed as directed in *Experiment I., Lesson XXXIII.* (p. 179).

Experiment II.—*To find the grams of iron in a solution of a ferric salt which is free, or almost free, from acid, using potassium permanganate as the standard solution.*

REACTION.—Zinc dust reduces neutral or slightly acid solutions of ferric salts to ferrous almost instantaneously; thus

$2\text{FeCl}_3\text{Aq} + \text{Zn dust} = 2\text{FeCl}_2\text{Aq} + \text{ZnCl}_2\text{Aq}$. If the solution is quite neutral a little FeO_2H_2 is precipitated, therefore the reaction should be conducted in a slightly acid liquid; much acid must be avoided, else the reduction is affected chiefly by the hydrogen evolved by the reaction of the acid and zinc (as in *Experiment I.*), and the process is very much slower.

The titration with permanganate cannot be conducted in the presence of the excess of zinc dust; therefore the liquid must be filtered from the unchanged zinc dust. Now, if the liquid were poured through an ordinary filter, some of the ferrous compound in solution would be oxidised to ferric by the atmospheric oxygen. To obtain a clear liquid for titration without any risk of oxidation being brought about by the air the device of *reversed filtration* is adopted.¹

A reversed filter is simply a piece of glass tubing about 75 mm. (3 inches) long and 35 mm. (say $1\frac{1}{2}$ inch) diameter, over one end of which is tied a piece of muslin; a piece of filter paper is put somewhat loosely over the muslin, and is tied (or fastened by a rubber band) round the tube. The piece of tubing is placed in the beaker containing the solution and the zinc dust, the end over which the filter paper is fastened being downwards; the liquid rises upwards in the tube, leaving the zinc dust behind, and a measured portion is drawn off by a pipette.

PROCESS.—Place 100 c.c. of the given solution of a ferric salt in a dry beaker; add about an eighth of a test-tubeful of zinc dust, and shake well; run in 5 or 10 c.c. dilute $\text{H}_2\text{SO}_4\text{Aq}$ (*quantity added must be measured accurately, and should not be more than 10 c.c.*); shake again, immerse a dry reversed filter in the liquid, withdraw 10 c.c. of the clear liquid that rises inside the filter, add a good deal of dilute $\text{H}_2\text{SO}_4\text{Aq}$, and titrate with standard $\text{K}_2\text{Mn}_2\text{O}_8\text{Aq}$. Repeat the titration twice, using 25 c.c. of the clear liquid that rises in the filter for each titration.

NORM.—The reaction is not affected by the quantity of water present; but if an unknown volume of water were introduced

¹ This method of reducing ferric salt solutions, for determination of the iron by permanganate, is due to Carnegie (*Chem. Soc. Journal*, 1888).

the calculation could not be made, because a portion only of the liquid is used for the titration, and, if the total volume of liquid is not known accurately, it would be impossible to tell what fraction of the total volume had been withdrawn for titration. Hence the beaker and the reversed filter used must be dry.

CALCULATION.—Suppose 100 c.c. of the ferric salt solution were taken, 5 c.c. of dilute $\text{H}_2\text{SO}_4\text{Aq}$ were added, 25 c.c. of the clear liquid were withdrawn, and 10 c.c. $\text{K}_2\text{Mn}_2\text{O}_8\text{Aq}$ were used for titration, 1 c.c. $\text{K}_2\text{Mn}_2\text{O}_8\text{Aq}$ being = .0056 gram iron; then the total liquid, a portion of which was used for the titration, measured 105 c.c., and would have used $\frac{105 \times 10}{25} = 42$ c.c.

$\text{K}_2\text{Mn}_2\text{O}_8\text{Aq}$. But this number of c.c. $\text{K}_2\text{Mn}_2\text{O}_8\text{Aq}$ was used to oxidise the iron in 100 c.c. of the *original solution*; hence, $\frac{42}{100} = .42$ c.c. $\text{K}_2\text{Mn}_2\text{O}_8\text{Aq}$ was used for the oxidation of the iron in 1 c.c. of the original solution; and, therefore, 1 c.c. of that solution contains $.42 \times .0056 = .00235$ gram iron.

NOTE.—This process may be used for solutions containing a good deal of $\text{H}_2\text{SO}_4\text{Aq}$. In such cases ammonia solution should be run, from a burette, into the acid solution, drop by drop, with constant shaking, until a *very faint* pp. is produced; the volume of ammonia solution must be noted. A small measured volume, say 10 c.c., dilute $\text{H}_2\text{SO}_4\text{Aq}$ should then be added, and the process continued as directed.

The results of the titrations by this method should be entered in your note-book in some such form as the following :—

1 c.c. standard $\text{K}_2\text{Mn}_2\text{O}_8\text{Aq}$ = grams iron.		
I.	II.	III.
c.c. ferric solution taken for the estimation.	c.c. $\text{H}_2\text{SO}_4\text{Aq}$ added.	c.c. liquid removed by pipette after reduction.
—	—	—

IV.

c.c. $K_2Mn_2O_8Aq$ used for titration of volume of reduced liquid in col. III.

—

VI.

Grams iron corresponding to c.c. $K_2Mn_2O_8Aq$ used for total volume of liquid.

—

V.

c.c. $K_2Mn_2O_8Aq$ that would be used for titration of total liquid (that is, c.c. in col. I. + c.c. in col. II.).

—

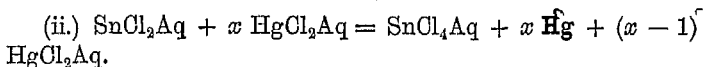
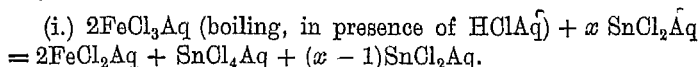
VII.

*Grams iron in 1 c.c. of ferric solution analysed;
= $\frac{\text{grams in col. VI.}}{\text{c.c. in col. I.}}$*

—

Experiment III.—*To find the grams of iron in a solution of a ferric salt containing hydrochloric acid, using potassium bichromate as the standard solution.*

REACTIONS.—The most convenient method of reduction in the present case is to add stannous chloride solution to the boiling solution of the ferric salt; and then to remove any excess of stannous chloride by adding mercuric chloride solution. If any stannous chloride were left in the solution it would react with some of the standard bichromate solution. The reactions may be represented as follows:—



Neither $SnCl_4Aq$ nor $HgCl_2Aq$ reacts with $K_2Cr_2O_7Aq$.

As this method of reduction is generally effected in a solution containing $HClAq$, it should not be employed when permanganate solution is used for the titration, because $HClAq$ and $K_2Mn_2O_8Aq$ interact with one another.

PROCESS.—To 25 c.c. of the ferric salt solution add a little hydrochloric acid, heat to boiling, and run stannous chloride solution, drop by drop, into the boiling liquid, until the liquid

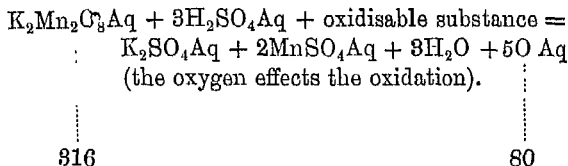
just becomes colourless (by proceeding thus any large excess of SnCl_2Aq is avoided); then remove the lamp, add a little mercuric chloride solution, and *at once* titrate by standard bichromate solution. Repeat the titration twice, using (i.) 10 c.c., (ii.) 25 c.c., of the original ferric solution.

CALCULATION.—Suppose 1 c.c. of the standard bichromate solution = .0056 gram iron. Let x = number of c.c. of this standard solution used to oxidise the iron in 25 c.c. of the solution after reduction; then $\frac{x \times .0056}{25}$ = grams of iron in 1 c.c. of the original solution.

NOTE ON NORMAL AND DECINORMAL SOLUTIONS OF POTASSIUM PERMANGANATE AND POTASSIUM BICHROMATE

These solutions are used for effecting oxidations. A normal solution of an oxidising agent is defined as a solution one litre whereof gives sufficient oxygen to oxidise one gram of hydrogen to water; that is, gives 8 grams of oxygen $\left[\frac{2\text{H}}{2} + \frac{\text{O}}{16} = \text{H}_2\text{O} \right]$.

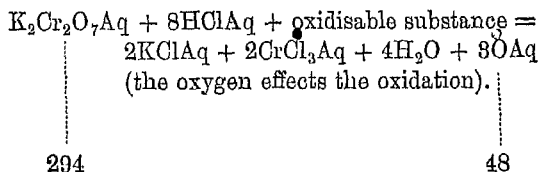
The reaction between potassium permanganate solution and an easily oxidisable substance, in presence of sulphuric acid, may be expressed by the following equation:—



From 316 grams $\text{K}_2\text{Mn}_2\text{O}_8$, in solution, are produced 80 grams of oxygen when the solution is used to effect oxidations in presence of acid; therefore 31.6 grams $\text{K}_2\text{Mn}_2\text{O}_8$ must be dissolved in one litre of water in order that this volume of solution shall give 8 grams of oxygen. Hence a normal solution of permanganate contains 31.6 grams, and a decinormal solution contains 3.16 grams, $\text{K}_2\text{Mn}_2\text{O}_8$ per litre.

The reaction between potassium bichromate solution and an

easily oxidisable substance, in presence of hydrochloric (or sulphuric) acid, may be expressed by this equation:—



From 294 grams $\text{K}_2\text{Cr}_2\text{O}_7$, in solution, are produced 48 grams of oxygen when the solution is used to effect oxidations in presence of acid; therefore a solution of $\text{K}_2\text{Cr}_2\text{O}_7$ containing $\frac{294}{6} = 49$ grams of this salt per litre will give 8 grams of oxygen, and will be (by definition) a normal solution.

It will be noticed that all the oxygen in $\text{K}_2\text{Mn}_2\text{O}_8$, in solution, is not available for effecting oxidations in volumetric analyses; nor is all the oxygen in $\text{K}_2\text{Cr}_2\text{O}_7$, in solution, available for this purpose; $\frac{5}{8}$ ths of the oxygen in the former salt, and $\frac{3}{4}$ ths of that in the latter salt, are available. It is customary to speak of that fraction of the total oxygen in these salts which effects oxidations, in the presence of acids, as *available oxygen*.

The strengths of normal and decinormal solutions of permanganate and bichromate may be stated in the following forms:—

$$1 \text{ c.c. N } \text{K}_2\text{Mn}_2\text{O}_8\text{Aq} = \cdot 0316 \text{ gram } \text{K}_2\text{Mn}_2\text{O}_8;$$

$$1 \text{ c.c. } \frac{\text{N}}{10} \text{K}_2\text{Mn}_2\text{O}_8\text{Aq} = \cdot 00316 \text{ gram } \text{K}_2\text{Mn}_2\text{O}_8.$$

$$1 \text{ c.c. N } \text{K}_2\text{Mn}_2\text{O}_8\text{Aq} = \cdot 008 \text{ gram oxygen};$$

$$1 \text{ c.c. } \frac{\text{N}}{10} \text{K}_2\text{Mn}_2\text{O}_8\text{Aq} = \cdot 0008 \text{ gram oxygen};$$

$$1 \text{ c.c. N } \text{K}_2\text{Mn}_2\text{O}_8\text{Aq} = \cdot 056 \text{ gram iron};$$

$$1 \text{ c.c. } \frac{\text{N}}{10} \text{K}_2\text{Mn}_2\text{O}_8\text{Aq} = \cdot 0056 \text{ gram iron}.$$

$$1 \text{ c.c. N } \text{K}_2\text{Cr}_2\text{O}_7\text{Aq} = \cdot 049 \text{ gram } \text{K}_2\text{Cr}_2\text{O}_7;$$

$$1 \text{ c.c. } \frac{\text{N}}{10} \text{K}_2\text{Cr}_2\text{O}_7\text{Aq} = \cdot 0049 \text{ gram } \text{K}_2\text{Cr}_2\text{O}_7;$$

$$1 \text{ c.c. N } K_2Cr_2O_7Aq = \cdot008 \text{ gram oxygen ;}$$

$$1 \text{ c.c. } \frac{N}{10} K_2Cr_2O_7Aq = \cdot0008 \text{ gram oxygen ;}$$

$$1 \text{ c.c. N } K_2Cr_2O_7Aq = \cdot056 \text{ gram iron ;}$$

$$1 \text{ c.c. } \frac{N}{10} K_2Cr_2O_7Aq = \cdot0056 \text{ gram iron.}$$

Notice that the sign = has different meanings in these statements: in the first and second statements it means 'contains'; in the third and fourth it means 'when used as an oxidiser, gives'; and in the fifth and sixth statements it means 'oxidises from ferrous to ferric iron.'

LESSON XXXV

EXERCISES ON THE ESTIMATION OF IRON COMPOUNDS

The following exercises are given as suggestions :—

Exercise I.—*Determine the grams of ferrous iron, and the grams of ferric iron, in 100 c.c. of the solution A.*

(i.) Determine the ferrous iron, by titration with standard permanganate or bichromate, in a measured volume of the solution.

(ii.) Reduce the ferric to ferrous iron, in another measured volume of the solution, and then determine the total iron.

Deduct the grams of ferrous iron in a stated volume of the solution from the grams of total iron in an equal volume of the solution, and the difference is ferric iron in that volume of the solution.

NOTE.—Test whether the solution is acid or neutral. If the solution is acid, and the acid present is sulphuric acid, put a little zinc dust into some of the solution; if there is a brisk effervescence, before estimating the total iron reduce, either by zinc as directed in *Experiment I. of Lesson XXXIV.*, or by nearly neutralising by ammonia and reducing by zinc dust as directed in *Experiment II. of Lesson XXXIV.* (see **NOTE** on p. 187). If the solution is strongly acid, and the acid present is hydrochloric, reduce by stannous chloride and titrate by bichromate (*Lesson XXXIV., Experiment III.*).

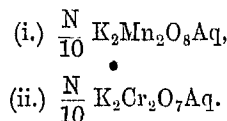
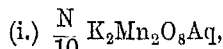
If the solution is neutral, reduce by zinc dust.

Exercise II.—(i.) *Find the weight of the small piece of pure iron wire given you without weighing it.*

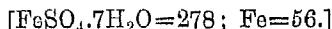
(ii.) *The solution B was prepared by dissolving 30 grams of ferrous sulphate crystals, $\text{FeSO}_4 \cdot x \text{H}_2\text{O}$, in a litre of water; find the value of x . [$\text{FeSO}_4 = 152$.]*

Exercise III.—The solution C was prepared by dissolving about 25 grams of partially oxidised ferrous sulphate crystals in a litre of very dilute sulphuric acid; how many grams of ferric iron (that is, iron in a ferric compound) were contained in the quantity of salt dissolved?

Exercise IV.—You are given a standard solution of ferrous sulphate; an unstandardised permanganate, and an unstandardised bichromate, solution; prepare about 100 c.c. of



Exercise V.—The solid D is ferric sulphate, $Fe_2(SO_4)_3$; when this solid is warmed with iron filings and diluted sulphuric acid for some time, a solution of ferrous sulphate is obtained. Prepare, from D, a solution of ferrous sulphate containing 0.03 gram of the salt $FeSO_4 \cdot 7H_2O$ per c.c.



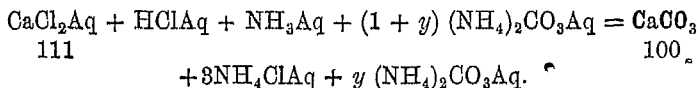
LESSON XXXVI.

ESTIMATION OF CALCIUM IN SOLUTIONS OF COMPOUNDS OF THAT METAL; GIVEN A STANDARD ACID SOLUTION AND A STANDARD ALKALI SOLUTION

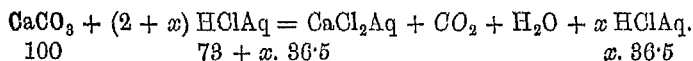
Apparatus and materials required.—Standard hydrochloric or nitric acid solution. Standard alkali solution. Methyl orange. Solution of a compound of calcium, the strength of which is known, but is not stated on the bottle. 250 c.c. and 500 c.c. measuring flasks. Burette. 100 c.c., 50 c.c., and 25 c.c., pipettes.

Experiment I.—*Determination of the grams of calcium chloride in a solution of calcium carbonate in diluted hydrochloric acid; given standard acid and alkali solutions.*

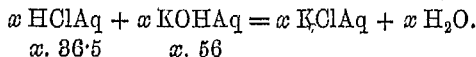
REACTIONS.—I. For the precipitation of calcium carbonate.



II. For the solution of the precipitated calcium carbonate in excess of standard HClAq.



III. For the titration, by standard potash solution, of the HClAq that has not reacted with the calcium carbonate.



A careful consideration of the first of these expressions of the chemical changes on which the process is based will show that addition of an excess of $(\text{NH}_4)_2\text{CO}_3\text{Aq}$ to a neutral solution

containing calcium chloride will precipitate the whole of the calcium as calcium carbonate, and that the other compounds present will remain in solution. Now, if the weight of calcium carbonate which is precipitated can be determined, it is easy to calculate the weight of calcium chloride in the volume of the solution taken for analysis, for 100 parts by weight of CaCO_3 are obtained from 111 parts by weight of CaCl_2 . The second equation tells that if the precipitated CaCO_3 is dissolved in a measured volume of HClAq , the weight of HCl in which is known, and which is more than sufficient to react with all the CaCO_3 , a definite weight of the HCl in that HClAq will react with the CaCO_3 , and the rest of the HCl will remain unchanged in the liquid. And the third equation tells that the weight of HCl which remains over when the reaction between the CaCO_3 and the HClAq is finished can be estimated by a standard potash solution.

PROCESS.—Transfer 50 c.c. of the solution of calcium carbonate in hydrochloric acid given you (that is, the solution of CaCl_2 in excess of HClAq) to a beaker; slowly pour down the side of the beaker (to prevent the spirting up of drops of liquid) dilute ammonia solution, *shaking constantly*, until the smell of ammonia is apparent (the whole of the acid in the liquid is thus neutralised); and then pour *cautiously* into the beaker three or four test-tubesful of a solution of ammonium carbonate. Now boil for a few minutes; allow the precipitated CaCO_3 to settle; then pour a *few drops* of ammonium carbonate solution down the side of the beaker, and observe whether this solution causes the formation of a pp. in the clear liquid. If a pp. does not form, an excess of ammonium carbonate has been added; in this case proceed to wash the pp. as directed in the next paragraph. If a pp. does form, more ammonium carbonate solution must be added, the contents of the beaker boiled, the pp. allowed to settle, and the test for complete precipitation repeated.

When the precipitation of CaCO_3 is completed, the next step is to wash the pp. until only pure CaCO_3 remains. Pour as much as you can of the clear liquid standing above the pp. down a glass rod (see fig. 2, p. 6), on to a filter carefully fitted into a

clean funnel, beneath which is placed a *clean* beaker; then pour *about a test-tubeful* of distilled water into the beaker containing the pp., boil for a few moments, let the pp. settle, and pour the clear supernatant liquid down the glass rod into the same filter as before. Repeat this process of washing three or four times; collect about half a test-tubeful of the last wash-water which runs through the filter, and test it for a *chloride*, by adding a drop of nitric acid and a very little silver nitrate solution (*compare* p. 67). If a chloride is present continue the process of washing, as directed, until a little of the wash-water ceases to give the reaction characteristic of chlorides. The pp. is now pure CaCO_3 ; if all NH_4ClAq has been washed away (see equation I. given on p. 194), you may be sure that all the $(\text{NH}_4)_2\text{CO}_3\text{Aq}$ has also been washed away; because $(\text{NH}_4)_2\text{CO}_3$ is more soluble in water than NH_4Cl .

Now place the beaker which contains the main part of the washed CaCO_3 under the filter, which contains a little of the washed CaCO_3 ; run 50 c.c. of the *standard* acid solution from a pipette on to the filter, allowing it to flow through the filter into the beaker (put the rod you used into the beaker, as a little CaCO_3 may be adhering to it), and shake the contents of the beaker. If the pp. does not completely dissolve run another 50 c.c. of the standard acid solution through the filter into the beaker, and shake the contents of the beaker. If the pp. is still not completely dissolved run 25 c.c. of the standard acid solution through the filter, as before. Proceed thus until every trace of the precipitated CaCO_3 has dissolved. Now remove the glass rod from the beaker, and wash it down, into the beaker, with distilled water; then pour two or three test-tubesful of distilled water through the filter, to wash the liquid that is adhering to the filter into the beaker (for this liquid will contain a little of the standard HClAq).

Now wash out a 250 c.c. measuring flask; place a clean funnel in the neck of the flask, and *cautiously* pour the liquid from the beaker into the flask; rinse the beaker repeatedly with distilled water, and pour the water each time into the measuring flask. Now pour distilled water into the measuring flask until the level of the liquid reaches exactly to the *containing mark* on

the neck of the flask. Put in the stopper, and mix the liquid in the flask *thoroughly*.

NOTE.—If the pp. of CaCO_3 was very large, you may have used so much standard acid solution to dissolve it that a 500 c.c. flask will be required.

Now withdraw 25 c.c. of the solution from the flask, add a few drops of *methyl orange* solution, and titrate with a standard alkali solution. Repeat the titration twice, using each time 50 c.c. of the liquid in the flask.

CALCULATIONS.—I. Find grams KOH used to neutralise the HCl in the whole of the 250 c.c. (or it may be 500 c.c.) of the liquid in the measuring flask; and from this calculate grams HCl neutralised by this weight of KOH . This gives grams HCl remaining unacted on by the CaCO_3 .

It is assumed that the standard acid was HClAq , and the standard alkali was KOH Aq .

II. Knowing the volume of standard HClAq poured on to the pp. of CaCO_3 , find the grams of HCl in this volume. This gives the total grams HCl added to the CaCO_3 .

III. Deduct grams HCl found in I. from grams HCl found in II. The difference is the grams HCl that reacted with the CaCO_3 .

IV. Knowing that 73 grams HCl react with 100 grams CaCO_3 , and that 100 grams CaCO_3 are obtained from 111 grams CaCl_2 , calculate the grams CaCl_2 in the volume of solution used for analysis.

State the final result as grams CaCl_2 per 100 c.c. of solution analysed.

NOTE ON CALCULATIONS WHEN NORMAL OR DECI-NORMAL SOLUTIONS ARE EMPLOYED

Calculations are very much shortened when normal or deci-normal (or pentanormal, or generally n -normal) solutions are employed in volumetric analyses; for x c.c. of any n -normal acid solution neutralises x c.c. of any n -normal alkali or alkaline carbonate solution, and x c.c. of any n -normal oxidising solution oxidises the same weight of an oxidisable substance as x c.c. of

any other n -normal oxidising solution. When n -normal solutions are employed it is not necessary to find the weights of the solid reagents that take part in the reactions until the last step of the calculation.

The following calculations of the results obtained in an analysis of a solution of calcium chloride will show the great shortening that is secured by using n -normal standard solutions:—

I.	II.	III.
<i>Volume of CaCl_2Aq taken</i>	<i>Volume of $\frac{N}{10} \text{HClAq}$ in which $\frac{\text{pp. of } \text{CaCO}_3}{\text{was dissolved}}$</i>	<i>Volume to which solution obtained in col. II. was made up</i>
50 cc.	125 c.c.	250 c.c.
IV.	V.	
<i>Volume of solution taken (from total vol. of 250 c.c.) for titration with alkali</i>	<i>Volume of $\frac{N}{10} \text{KOH Aq}$ used to neutralise solution noted in col. IV. (Mean of 3 titrations)</i>	
50 c.c.	15.5 c.c.	

Calculations by method already described.—

(i.)	(ii.)
Vol. of standard KOH Aq required to neutralise HCl in total 250 c.c. of col. III.	Grams KOH required to neutralise HCl in total 250 c.c. of col. III.
$\frac{15.5 \times 250}{50} = 77.5 \text{ c.c.}$	$77.5 \times .0056 = .4340 \text{ gram.}$
(iii.)	(iv.)
Grams HCl neutralised by grams KOH in col. (ii.)	Grams HCl in solution in which CaCO_3 was dissolved
$\frac{36.5 \times .434}{56} = .2829 \text{ gram.}$	$125 \times .00365 = .45625 \text{ gram.}$
= weight of HCl not acted on by CaCO_3 .	

(v.)

Grams HCl that reacted
with $CaCO_3$ precipitated from
50 c.c. of solution analysed
 $\cdot 45625 - \cdot 2829 = \cdot 17335$ gram.

(vi.)

Grams $CaCl_2$ in 50 c.c. of
solution analysed
 $\frac{\cdot 17335 \times 111}{73} = \cdot 26359$ gram.

Calculations by shorter method.—The solutions of $HClAq$ and $KOHAq$ used were $\frac{N}{10}$, therefore 1 c.c. of one neutralises 1 c.c. of the other. Moreover, as 1 c.c. $\frac{N}{10}$ $HClAq$ (containing $\cdot 00365$ gram HCl) reacts with $\cdot 005$ gram $CaCO_3$ (73 grams HCl react with 100 grams $CaCO_3$), and is, therefore, equivalent in the reactions of this analysis to $\cdot 00555$ gram $CaCl_2$ (100 grams $CaCO_3$ are obtained from 111 grams $CaCl_2$), it follows that

(number of c.c. of $\frac{N}{10}$ $HClAq$ used to react with all the $CaCO_3$
precipitated from 50 c.c. of the $CaCl_2Aq$) $\times \cdot 00555 =$
gram $CaCl_2$ in 50 c.c. of solution analysed.

Now, as the whole of the $CaCO_3$ precipitated from 50 c.c. of the $CaCl_2Aq$ was dissolved in 125 c.c. $\frac{N}{10}$ $HClAq$, and as the $HClAq$ remaining unacted on by the $CaCO_3$ used 77.5 c.c. $\frac{N}{10}$ $KOHAq$ for neutralisation, it follows that $125 - 77.5 = 47.5$ c.c. $\frac{N}{10}$ $HClAq$ were used to react with the $CaCO_3$ precipitated; hence $47.5 \times \cdot 00555 = \cdot 2636$ gram $CaCl_2$ was contained in 50 c.c. of the solution analysed.

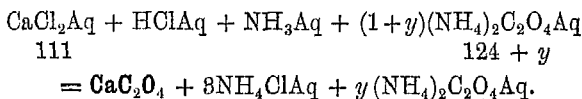
LESSON XXXVII

ESTIMATION OF CALCIUM IN SOLUTIONS OF COMPOUNDS OF THAT METAL; GIVEN A STANDARD PERMANGANATE SOLUTION, AND A STANDARD AMMONIUM OXALATE SOLUTION.

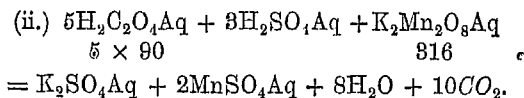
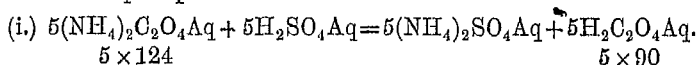
Apparatus and materials required.—Standard permanganate solution. Standard ammonium oxalate solution. Solution of a compound of calcium, the strength of which is known but is not stated on the bottle. 250 c.c. measuring flask. Burette. 100 c.c., 50 c.c., and 25 c.c., pipettes.

Experiment I.—*Determination of the grams of calcium chloride in a solution of that salt; given standard permanganate and ammonium oxalate solutions.*

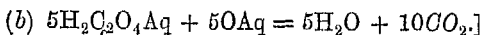
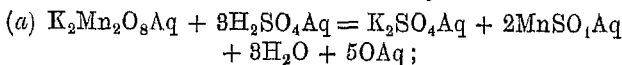
REACTIONS.—I. For precipitation of calcium oxalate.



II. For titration of ammonium oxalate solution remaining over when precipitation is finished.



[The second of the reactions under heading II. may be supposed to occur in two stages simultaneously :



The estimation, by permanganate, of oxalic acid, or an oxalate in solution, has not been considered in former lessons. The process is an oxidation; it proceeds rapidly at a temperature of about 60° , but very slowly at the ordinary temperature; the end of the reaction is marked by the production of a faint pink colour in the liquid, due to the persistence unchanged of the next drop of permanganate solution which is added after the chemical change is finished.

The equations indicate that if a measured volume of standard $(\text{NH}_4)_2\text{C}_2\text{O}_4\text{Aq}$, containing more than sufficient $(\text{NH}_4)_2\text{C}_2\text{O}_4$ to react with all the CaCl_2 in a neutral solution of that salt, is added to a measured volume of the CaCl_2Aq , and if the $(\text{NH}_4)_2\text{C}_2\text{O}_4$ which remains unchanged in the liquid above the precipitated CaC_2O_4 is estimated by titration with standard $\text{K}_2\text{Mn}_2\text{O}_8\text{Aq}$, it is possible to calculate the weight of CaCl_2 in the volume of the CaCl_2Aq used for analysis.

PROCESS.—By means of a pipette, measure 50 c.c. of the solution of the calcium compound given you into a *clean* 250 c.c. measuring flask; add about 10 c.c. dilute ammonia solution, shake, and find whether the liquid smells of ammonia. If there is a smell of ammonia the liquid is alkaline; in this case proceed to the next stage of the analysis. If there is not a smell of ammonia, add about another 10 c.c. of dilute ammonia solution, and mix by shaking. Proceed thus till the liquid is slightly alkaline.

Why must the solution be made alkaline?

Now run in 100 c.c. of the standard $(\text{NH}_4)_2\text{C}_2\text{O}_4\text{Aq}$, put in the stopper of the flask, *shake the flask vigorously for about half a minute*, and let the pp. settle; when the liquid above the pp. is fairly clear allow 10 c.c. of the standard $(\text{NH}_4)_2\text{C}_2\text{O}_4\text{Aq}$ to flow gently into the flask, and observe whether a pp. is produced thereby. If precipitation does not occur, proceed to the next stage of the analysis; but if the 10 c.c. of the standard $(\text{NH}_4)_2\text{C}_2\text{O}_4\text{Aq}$ produce a pp., add 50 c.c. of the standard $(\text{NH}_4)_2\text{C}_2\text{O}_4\text{Aq}$, *shake vigorously for at least half a minute*, let the pp. settle, and test whether precipitation is completed by allowing 10 c.c. of the standard $(\text{NH}_4)_2\text{C}_2\text{O}_4\text{Aq}$ to flow gently

into the flask. When the process of precipitation is completed, note the total volume of standard $(\text{NH}_4)_2\text{C}_2\text{O}_4\text{Aq}$ that has been added, fill up the flask to the *containing mark* with water, insert the stopper, *shake vigorously for some time*, and set the flask aside till the pp. has settled *completely*. (While the settling process is going on, consider the calculations set out below.)

When the precipitated CaC_2O_4 has settled *completely*, carefully suck up 25 c.c. of the clear supernatant liquid; *without disturbing the pp.*, by a *dry* pipette, and transfer it to a clean beaker; repeat this process twice, so that you have three quantities of the clear liquid, of 25 c.c. each, in separate beakers. Add about two or three test-tubesful of diluted sulphuric acid to each beaker, heat to about 60° (till the beaker is comfortably warm to the touch), and run standard $\text{K}_2\text{Mn}_2\text{O}_8\text{Aq}$ into each beaker until a faint pink colour persists in the liquid for a minute or two.

NOTE.—If the precipitated CaC_2O_4 does not settle *completely* in a reasonable time, fit a *dry* filter, made of specially good paper, into a *dry* funnel, place a clean *dry* beaker under the funnel, and pour the liquid above the pp. through the filter, without disturbing the pp.; you will thus obtain a clear liquid for titration. The filter, funnel, and beaker must be dry, because if an unknown volume of water were brought into the liquid the total volume of the liquid would be unknown, and hence you would not know what fraction of the total liquid you had taken for the titration with permanganate solution.

CALCULATIONS.—*First method.* I. Find the total weight in grams of the $(\text{NH}_4)_2\text{C}_2\text{O}_4$ added to the solution of the calcium compound.

II. Find the weight in grams of $(\text{NH}_4)_2\text{C}_2\text{O}_4$ in the *whole of the liquid* above the precipitated CaC_2O_4 .

III. Deduct the grams of $(\text{NH}_4)_2\text{C}_2\text{O}_4$ found in II. from the grams of the same salt found in I.; the difference is the grams of $(\text{NH}_4)_2\text{C}_2\text{O}_4$ that have reacted with the calcium compound in the volume of the solution analysed.

IV. Knowing (see equation under *Reaction I.*, p. 200) that 124 grams of $(\text{NH}_4)_2\text{C}_2\text{O}_4$ react with 111 grams of CaCl_2 (in solu-

tion), calculate, from the results of III., the grams of CaCl_2 in the volume of the solution analysed. [If the calcium compound was some compound other than the chloride the calculation is easily modified.]

• The following example will illustrate this method of calculation :—

$$\frac{N}{10} \text{K}_2\text{Mn}_2\text{O}_8\text{Aq used; } 1 \text{ c.c.} = .00316 \text{ gram } \text{K}_2\text{Mn}_2\text{O}_8;$$

therefore, $1 \text{ c.c.} = .00124 \times 5 = .0062 \text{ gram } (\text{NH}_4)_2\text{C}_2\text{O}_4$.

Strength of $(\text{NH}_4)_2\text{C}_2\text{O}_4\text{Aq}$ used; $1 \text{ c.c.} = .00565 \text{ gram } (\text{NH}_4)_2\text{C}_2\text{O}_4$.

[Notice the different meanings of the sign = in these statements.]

50 c.c. CaCl_2Aq taken; NH_3Aq added, and 100 c.c. standard $(\text{NH}_4)_2\text{C}_2\text{O}_4\text{Aq}$ run in; addition of 10 c.c. more standard $(\text{NH}_4)_2\text{C}_2\text{O}_4\text{Aq}$ did not produce any pp., therefore, total volume of standard $(\text{NH}_4)_2\text{C}_2\text{O}_4\text{Aq}$ added = 110 c.c.; flask filled to mark (250 c.c.) with water, shaken, and set aside; 25 c.c. of clear liquid titrated with $\frac{N}{10} \text{K}_2\text{Mn}_2\text{O}_8\text{Aq}$ used (i.) 5.3 c.c., (ii.) 5.4 c.c., (iii.)

5.4 c.c.—mean = 5.37 c.c.—of the $\frac{N}{10} \text{K}_2\text{Mn}_2\text{O}_8\text{Aq}$.

• Total grams of $(\text{NH}_4)_2\text{C}_2\text{O}_4$ added = $110 \times .00565 = .6215$ gram.

Grams of $(\text{NH}_4)_2\text{C}_2\text{O}_4$ in the 25 c.c. of clear liquid taken out of the 250 c.c. = $.0062 \times 5.37 = .03329$ gram; therefore, grams of $(\text{NH}_4)_2\text{C}_2\text{O}_4$ remaining unacted on in the whole volume (250 c.c.) of liquid = $.03329 \times \frac{250}{25} = .3329$ gram.

Grams of $(\text{NH}_4)_2\text{C}_2\text{O}_4$ that reacted with the CaCl_2 in the 50 c.c. of CaCl_2Aq taken for analysis = $.6215 - .3329 = .2886$ gram.

Grams of CaCl_2 in the 50 c.c. CaCl_2Aq taken for the estimation = $\frac{111 \times .2886}{124} = .2582$ gram.

Result.—100 c.c. of the CaCl_2Aq contain $.2582 \times 2$

= 5.164 gram CaCl_2 ; or, 1 litre of the CaCl_2Aq contains 5.164 grams CaCl_2 .

Second, and shorter, method of calculation:—

Standard $(\text{NH}_4)_2\text{C}_2\text{O}_4\text{Aq}$; 1 c.c. = .00565 gram $\text{NH}_4\text{C}_2\text{O}_4$.

Now, 1 c.c. $\frac{\text{N}}{10} (\text{NH}_4)_2\text{C}_2\text{O}_4\text{Aq}$ = .0062 gram $(\text{NH}_4)_2\text{C}_2\text{O}_4$; therefore, 1 c.c. standard $(\text{NH}_4)_2\text{C}_2\text{O}_4\text{Aq}$ used = $\frac{.00565}{.0062} = .911$ c.c. $\frac{\text{N}}{10} (\text{NH}_4)_2\text{C}_2\text{O}_4\text{Aq}$.

$\left[\frac{\text{N}}{10} (\text{NH}_4)_2\text{C}_2\text{O}_4\text{Aq} \right]$ contains that number of grams of $(\text{NH}_4)_2\text{C}_2\text{O}_4$ per litre which is oxidised by .8 gram oxygen; the equations on p. 200 show that this weight is 6.2 gram $(\text{NH}_4)_2\text{C}_2\text{O}_4$.]

1 c.c. $\frac{\text{N}}{10} \text{K}_2\text{Mn}_2\text{O}_8\text{Aq}$ oxidises 1 c.c. $\frac{\text{N}}{10} (\text{NH}_4)_2\text{C}_2\text{O}_4\text{Aq}$.

1 c.c. $\frac{\text{N}}{10} (\text{NH}_4)_2\text{C}_2\text{O}_4\text{Aq}$ reacts with .00555 gram CaCl_2 in solution (for 124 grams $(\text{NH}_4)_2\text{C}_2\text{O}_4 = 111$ grams CaCl_2).

Number of c.c. of $\frac{\text{N}}{10} (\text{NH}_4)_2\text{C}_2\text{O}_4\text{Aq}$ added to 50 c.c. $\text{CaCl}_2\text{Aq} = 110 \times .911 = 100.2$ c.c.

Number of c.c. of $\frac{\text{N}}{10} (\text{NH}_4)_2\text{C}_2\text{O}_4\text{Aq}$ that remained unacted on by CaCl_2 in 50 c.c. $\text{CaCl}_2\text{Aq} = 5.87 \times \frac{250}{25} = 58.7$ c.c.

Number of c.c. of $\frac{\text{N}}{10} (\text{NH}_4)_2\text{C}_2\text{O}_4\text{Aq}$ that reacted with CaCl_2 in 50 c.c. $\text{CaCl}_2\text{Aq} = 100.2 - 58.7 = 46.5$ c.c.

Therefore, the weight of CaCl_2 present in 50 c.c. of the CaCl_2Aq = $46.5 \times .00555 = .2581$ gram.

Result.—100 c.c. of the CaCl_2Aq contain $.2581 \times 2 = .5162$ gram CaCl_2 , or 1 litre of the CaCl_2Aq contains 5.162 grams CaCl_2 .

When a standard solution is not *n*-normal, it is very con-

venient to calculate the factor by which 1 c.c. must be multiplied to convert it into 1 c.c. of an n -normal solution.

The methods used in *Lessons XXXVI. and XXXVII.* for estimating compounds of calcium may be applied for the estimations of some other metals. Metals completely precipitable as carbonates, which carbonates can be washed without undergoing change, and can then be dissolved in very dilute acid solution, may be estimated, generally, by the method used in *Lesson XXXVI.* Metals completely precipitable as oxalates can be estimated, generally, by the method used in *Lesson XXXVII.*

The processes used in *Lessons XXXVI. and XXXVII.* are illustrations of methods which are often employed in volumetric analyses; namely, the accomplishment of a reaction by an excess of a standard solution, followed by the estimation of the quantity of the standard solution which remains over when the reaction is completed.

LESSON XXXVIII

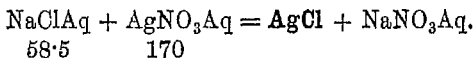
ESTIMATION OF CHLORINE IN SOLUTIONS OF CHLORIDES,
BY MEANS OF STANDARD SILVER SOLUTION

Apparatus and materials required.—Standard solution of silver nitrate. Solution of sodium chloride, and solution of hydrochloric acid; the strengths of these are known, but are not stated on the bottles. Nearly saturated solution of potassium chromate. Pure calcium carbonate. Burette. 10 c.c. and 25 c.c. pipettes.

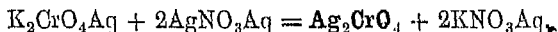
Piece of glass tubing about 150 mm. (6 inches) long drawn to fine opening at one end.

Experiment I.—*Determination of weight of common salt in one litre of an aqueous solution thereof; given standard silver nitrate solution.*

REACTIONS.—I. Reaction between sodium chloride and silver nitrate in aqueous solutions.



II. Reaction between potassium chromate and silver nitrate in aqueous solutions.



Silver chloride (AgCl) is white, and silver chromate (Ag_2CrO_4) is red. If an aqueous solution of silver nitrate is added slowly to an aqueous solution of sodium chloride containing a few drops of an aqueous solution of potassium chromate, the liquid being constantly shaken, the production of a red pp. of Ag_2CrO_4 does not occur until the reaction between the NaClAq and the AgNO_3Aq is completed. Hence it is easy to determine the

close of the reaction between the NaClAq and the AgNO_3Aq by using $\text{K}_2\text{CrO}_4\text{Aq}$ as the indicator.

PROCESS.—To 10 c.c. of the NaClAq given you, in a beaker placed on white paper, add a little water, and two or three drops of a nearly saturated solution of potassium chromate. A piece of glass tubing narrowed at one end is used for dropping in the $\text{K}_2\text{CrO}_4\text{Aq}$.

Now run the standard AgNO_3Aq slowly, from a burette, into the beaker, *shaking the beaker constantly*, until the pp. which at first is white assumes a faint reddish buff colour. Repeat the titration twice, using (i.) 10 c.c., and (ii.) 25 c.c., of the NaClAq .

The titrations must be conducted in cold solutions.

CALCULATIONS.—I. From volume of standard AgNO_3Aq used calculate grams of AgNO_3 used; then apply data given by the first equation, that 170 grams AgNO_3 react with 58.5 grams NaCl , to find grams of NaCl in volume of NaClAq used for analysis.

II. Suppose standard AgNO_3Aq to be *decinormal*.

1 c.c. $\frac{\text{N}}{10}$ AgNO_3Aq contains .0170 gram $\text{AgNO}_3 = .0108$ gram Ag ; that is, the weight of AgNO_3 (or Ag) which reacts with .00855 gram chlorine, which is the weight of chlorine that combines with .0001 gram hydrogen.

[A normal solution of chlorine contains 35.5 grams Cl per litre, exactly sufficient to combine with 1 gram of hydrogen; therefore $\frac{\text{N}}{10}$ chlorine solution contains 3.55 grams Cl per litre = .00855 gram Cl per c.c.]

Then, as 170 grams AgNO_3 react with 58.5 grams NaCl , it follows that 1 c.c. $\frac{\text{N}}{10}$ $\text{AgNO}_3\text{Aq} = .00585$ gram $\text{NaCl} = .00585$ gram Cl ; therefore, number of c.c. of $\frac{\text{N}}{10}$ AgNO_3Aq used $\times .00585$ = gram NaCl in volume of NaClAq used for analysis.

Suppose standard AgNO_3Aq to be of this strength:

$$1 \text{ c.c.} = .0185 \text{ gram } \text{AgNO}_3.$$

or three drops of nearly saturated K_2CrO_4 Aq, and run standard $AgNO_3$ Aq, from a burette, *slowly* into the beaker, *shaking constantly*, until the pp., which at first is white, assumes a faint reddish buff colour.

• Repeat the process twice, using in one case 10 c.c., and in the other case 25 c.c., of the HCl Aq.

CALCULATIONS.—I. From volume of standard $AgNO_3$ Aq used calculate grams of $AgNO_3$ used; then apply data given by the equations, that 170 grams $AgNO_3$ react with 86.5 grams HCl , to find grams HCl in volume of HCl Aq used for analysis.

II. Suppose the standard $AgNO_3$ Aq to be *decinormal*. Then number of c.c. $\frac{N}{10}$ $AgNO_3$ Aq used $\times .00865$ = grams HCl in volume of HCl Aq used for analysis.

III. Suppose the standard $AgNO_3$ Aq not to be *decinormal*. Find factor by which 1 c.c. of the standard solution used must be multiplied to give volume of $\frac{N}{10}$ solution equivalent to 1 c.c. of the standard solution. Then number of c.c. standard solution used $\times .00865 \times$ factor = grams HCl in volume of HCl Aq used for analysis.

LESSON XXXIX.

EXERCISES ON THE ESTIMATION OF CALCIUM COMPOUNDS,
CHLORIDES, AND ACIDS

The following exercises are given as suggestions.

Exercise I.—*The liquid A is a solution of sodium chloride in very dilute hydrochloric acid; find the grams of NaCl and the grams of HCl in 100 c.c. of A.*

(i.) Determine HCl by titration with standard alkali, [HCl = 36.5.]

(ii.) Determine total chlorine by method given in *Experiment II., Lesson XXXVIII.* [NaCl = 58.5] (p. 208.)

Exercise II.—*The liquid B is a solution of calcium carbonate in very dilute nitric acid; find the grams of $\text{Ca}(\text{NO}_3)_2$ and the grams of HNO_3 in one litre of B. [$\text{Ca}(\text{NO}_3)_2 = 164$; $\text{HNO}_3 = 63$.]*

(i.) Determine HNO_3 by titration with standard alkali.

(ii.) Determine $\text{Ca}(\text{NO}_3)_2$ by estimating calcium by the method described in *Lesson XXXVI.*, or by that described in *Lesson XXXVII.* (pp. 194, 200.)

Exercise III.—*Determine the weight of the specimen of pure calcium carbonate C without weighing it.* [$\text{CaCO}_3 = 100$.]

Exercise IV.—*The liquid D was prepared by dissolving x grams of calcium oxalate (CaC_2O_4) in diluted sulphuric acid; what was the value of x?* [$\text{CaC}_2\text{O}_4 = 128$.]

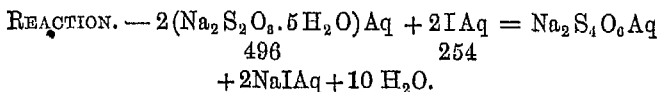
• LESSON XL

ESTIMATION OF IODINE IN SOLUTION BY MEANS OF A STANDARD
SOLUTION OF SODIUM THIOSULPHATE

Apparatus and materials required.—Standard $\text{Na}_2\text{S}_2\text{O}_3\text{Aq.}$ Solution of iodine in KIAq. the strength of which is known but is not stated on the bottle. Powdered starch. Burette. Pipettes to deliver 10 c.c. and 25 c.c.

• **Experiment I.**—*Given a dilute solution of iodine in potassium iodide solution and a standard solution of sodium thiosulphate; find the strength of the solution of iodine.*

Sodium thiosulphate is a white crystalline salt, easily soluble in water; the composition of the crystals is $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$. An aqueous solution of this salt reacts with iodine in solution to form sodium tetrathionate and sodium iodide, both of which remain in solution in the water. A little iodine in solution gives a blue colour with thin starch paste, which is prepared by boiling a *very little* starch with water; a solution containing a fair quantity of iodine gives a greenish brown colour with starch paste. None of the three salts, sodium thiosulphate, sodium tetrathionate, or sodium iodide, affects the colour of starch paste.



PROCESS.—Place 10 c.c. of the iodine solution in a beaker standing on white paper, add two or three test-tubesful of distilled water, and run the standard thio solution¹ into the liquid

¹ Solution of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ is usually called '*thio solution*' in volumetric analysis.

till the colour thereof is pale yellow (that is, until only a little free iodine remains unacted on). Then grind a piece of starch about the size of a pea with a *very little* water in a mortar, pour into about two test-tubefuls of *boiling* water, allow to settle, and decant the clear liquid. Add about a dozen drops of this thin, clear, starch paste to the contents of the beaker; and continue the *slow* addition of the standard thio solution, *shaking constantly*, until the blue colour of the liquid just vanishes.

Repeat the titration twice, using in one case 10 c.c., and in the other case 25 c.c., of the iodine solution.

CALCULATION.—I. Find grams of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ added; then, knowing (from the equation) that 248 grams $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ react with 127 grams iodine, calculate grams of iodine in the volume of iodine solution used for analysis.

II. Suppose the thio solution to be *decinormal* (see NOTE). Then number of c.c. of $\frac{N}{10} \text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{OAq}$ used $\times \cdot 0127 =$ grams iodine in volume of iodine solution used for analysis.

III. If the thio solution is not decinormal. Find factor by which 1 c.c. thio solution must be multiplied to give equivalent volume of $\frac{N}{10}$ thio solution (see NOTE). Then number of c.c. standard thio solution used $\times \cdot 0127 \times \text{factor} =$ grams iodine in volume of iodine solution used for analysis.

NOTE.—*Normal and decinormal thio and iodine solutions.*—One litre of a normal iodine solution contains that weight of iodine in grams which will combine with one gram of hydrogen; this weight is 127 grams. One litre of a normal thio solution contains that weight of sodium thiosulphate in grams which will react with 127 grams of iodine; this weight is 248 grams of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$. The strength of a thio solution is usually stated in terms of the number of grams of iodine with which 1 c.c. of the thio solution reacts; for thio solution is always used for measuring quantities of iodine.

The following statements present the strengths of N and $\frac{N}{10}$ solutions of iodine and sodium thiosulphate:—

1 c.c. N iodine solution = .127 gram iodine ;

1 c.c. $\frac{N}{10}$ iodine solution = .0127 gram iodine.

1 c.c. N iodine solution = .248 gram $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$;

1 c.c. $\frac{N}{10}$ iodine solution = .0248 gram $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$.

1 c.c. N thio solution = .248 gram $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$;

1 c.c. $\frac{N}{10}$ thio solution = .0248 gram $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$.

1 c.c. N thio solution = .127 gram iodine ;

1 c.c. $\frac{N}{10}$ thio solution = .0127 gram iodine.

Notice the different meanings of the sign = in these statements.

A COURSE OF PRACTICAL CHEMISTRY

PART I

ELEMENTARY

SECTION III

Qualitative Analysis

IN the first section of this course we have noticed that a substance is often recognised by means of its physical properties; for instance, salammoniac was distinguished from some other substances by the fact that it sublimed readily when heated in a dry test-tube (*Lesson I., Experiment II.*, p. 3), and this property was used (*Lesson I., Experiment III.*, p. 4) to separate salammoniac from a mixture of that substance and sand; water was recognised by its appearance, taste, and boiling point (*Lesson X., Experiment I.*, p. 49).

We have also been able to identify certain substances by causing them to undergo change into other substances the properties of which are readily recognised; for instance, a heavy red powder was found to be changed by heat into mercury, which was recognised by its appearance, and oxygen, which caused a glowing chip of wood to burn brightly (*Lesson V., Experiment IV.*, p. 25); and a liquid was found to contain iodine by the fact that the addition to it of a drop of starch paste produced a blue colour (*Lesson XXVII., Experiment I.*, p. 127); again, a certain odourless, colourless gas, wherein a burning taper went out, was distinguished from another similar gas,

which also extinguished a burning taper, by the fact that the former gas (nitrogen) did not produce any visible change in lime water, whereas a white solid was formed when the latter gas (carbon dioxide) was shaken with lime water (*Lesson II., Experiment I., and Lesson VII., Experiment II., pp. 8 and 29*).

In *Lesson XI., Experiment I.*, the salt prepared by neutralising an aqueous solution of basic potassium oxide by a solution of acidic sulphur trioxide was shown to be a compound of potassium by observing that a violet colour was imparted to a hot non-luminous flame wherein a little of the salt was volatilised (p. 54). In *Lesson XV., Experiment I.*, a salt was formed by dissolving copper in nitric acid and evaporating; and an aqueous solution of this salt was found to turn blue when excess of ammonia was added to it (p. 69). Now experiments show that the volatilisation of any compound of potassium in a non-luminous flame colours the flame violet, and that the addition of an excess of ammonia to a solution of any compound of copper causes the solution to become blue. The first of these reactions is used as a means for detecting compounds of potassium; and the second as a means for detecting compounds of copper.

By making a systematic comparison of the properties and reactions of the compounds of the different elements it becomes possible to select certain properties and reactions whereby the compounds of one element can be distinguished from those of the other elements. Qualitative analysis rests on the comparative study of the properties and reactions of the elements and their compounds; and systematic qualitative analysis begins when elements and compounds are examined with the object of finding properties and reactions which distinguish elements, and compounds of elements, from one another, and properties and reactions which serve to detect the constituents of mixtures of elements or mixtures of compounds.

The immediate objects of qualitative analysis are (1) the determination of the qualitative composition of mixtures of elements, such as a mixture of copper and zinc in a certain alloy (brass), or a mixture of oxygen and nitrogen in air; (2) the determination of the qualitative composition of compounds, such

as water, chalk, oil of vitriol, or common salt; and (8) the determination of the qualitative composition of mixtures of compounds, such as ironstone, felspar, dolomite, mineral water, or bleaching powder.

To determine the ultimate qualitative composition of a mixture of elements, or of a compound—for mixtures of compounds may always be resolved into two or more compounds—means, then, to find of what elements the mixture, or the compound, is composed, without determining the quantities of those elements that can be obtained from a determinate quantity of the compound or the mixture.

But the problem of qualitative analysis is somewhat more restricted in ordinary practice than this. Systematic qualitative analysis may be said, without much exaggeration, to be restricted to the examination of alloys and salts, using the term *salt* in its widest acceptance to include acids, bases, and the compounds more strictly called salts; and the study of the methods used for the qualitative analysis of salts includes the study of the methods used for the detection of the elementary constituents of alloys.

Salts are generally prepared by the combination of elements, by the interaction of acidic and basic oxides, by the interaction of metallic oxides or hydroxides and acids, by the interaction of metals and acids, by the interaction of salts and acids, and by the interaction of salts and salts. (For examples, see Synopsis of Methods for Preparing Salts, pp. 140–142). All the salts prepared by these methods, and indeed all salts, may be regarded, and for the purposes of qualitative analysis are regarded, as composed of two parts: a *metallic radicle*, and an *acidic radicle*. In almost every case the metallic radicle is an element—a metal; for instance, there are salts of copper, salts of iron, salts of lead, of tin, and so on. The commonest exception to this statement is found in the salts of the compound radicle ammonium (NH_4). The acidic radicle of a salt is sometimes a non-metal, as in chlorides, bromides, and iodides; but more frequently it is a group of non-metals, as in nitrates (compounds of NO_3), sulphates (compounds of SO_4), carbonates (compounds of CO_3), or phosphates (compounds of PO_4); in some cases the

acidic radicle of a salt is a group of non-metals (or a non-metal) and a metal, as in ferrocyanides (compounds of $\text{Fe}[\text{CN}]_6$), chromates (compounds of CrO_4), or permanganates (compounds of Mn_2O_8). Double salts may be composed of two metals and an acidic radicle, as potash alum $\text{K}_2\text{Al}_2(\text{SO}_4)_4 \cdot 24\text{H}_2\text{O}$, or of two metals and two acidic radicles, as the mixed alum $\text{K}_2\text{Al}_2(\text{SO}_4)_3(\text{SeO}_4) \cdot 24\text{H}_2\text{O}$.

Acids are included in the foregoing description of salts; as an acid may be regarded, and for the purposes of qualitative analysis is regarded, as composed of hydrogen—representing the metallic radicle of the salt—and an acidic radicle; for instance, hydrochloric acid ($\text{H}.\text{Cl}$), sulphuric acid ($\text{H}_2.\text{SO}_4$), nitric acid ($\text{H}.\text{NO}_3$), and permanganic acid ($\text{H}_2.\text{Mn}_2\text{O}_8$). Bases are also included in the foregoing description of salts; as, for the purposes of qualitative analysis, a base is regarded as a compound of a metal and hydroxyl (OH); for instance, potash ($\text{K}.\text{OH}$), baryta ($\text{Ba}.\text{OH}_2$), and ferric hydroxide ($\text{Fe}.\text{OH}_3$).

The metallic radicles of salts will be referred to hereafter, in the directions given for analysis, as the metals of the salts.

The primary object of the qualitative analysis of a salt is, then, to discover of what metal (or metals), and what acidic radicle (or radicles), the salt is composed; or, in the case of the analysis of a mixture of salts, to determine what metals and what acidic radicles compose the compounds that form the mixture.

The analyst cannot determine by qualitative methods (except in a few special cases) what salts are present in a mixture of salts; he can only detect the metals and the acidic radicles of which these salts are composed. For instance, the results obtained in the qualitative analysis of a mixture of ferric sulphate, magnesium nitrate, and sodium chloride are the same as the results obtained in the qualitative analysis of a mixture of ferric nitrate, magnesium chloride, and sodium sulphate, or of a mixture of any salts that can be formed by the combination of the three metals, iron, magnesium, and sodium, with the radicles of the three acids, nitric, hydrochloric, and sulphuric. A solution of any three salts formed by combining iron, magnesium, and sodium with the three acidic radicles NO_3 , Cl , and SO_4 , behaves

towards the reagents used in qualitative analysis as if it were a solution of six radicles, three of which are metallic—Fe, Mg, and Na—and three are acidic— NO_3 , Cl, and SO_4 . Similarly, an aqueous solution of a double salt behaves towards the reagents used in qualitative analysis as if it were a mixture of the metallic and acidic radicles that compose the salt; for instance, a solution of potash alum ($\text{K}_2\text{Al}_2(\text{SO}_4)_4 \cdot 24\text{H}_2\text{O}$) reacts in qualitative analysis as a solution of the metallic radicles K and Al, and the acidic radicle SO_4 .

The reactions of qualitative analysis, as well as many other reactions and properties of salts, find a simple and consistent explanation in terms of the hypothesis that when salts are dissolved in much water they are separated, more or less completely, into their metallic and acidic radicles, and that these radicles exist in the aqueous solutions of salts, each metallic radicle carrying a charge of positive electricity, and each acidic radicle a charge of negative electricity. According to this view salts are electrolytes, and most of the reactions made use of in analytical chemistry are the reactions of the *ions* of these electrolytes. As we proceed we shall find that most of the reactions we have to employ in the detection of metals and acidic radicles are reactions between solutions of salts and salts, or salts and acids, or salts and alkalis. A fairly dilute aqueous solution of a compound of any of these classes is regarded by the *electrolytic ionisation theory* as containing the ions into which the compound is primarily separated by an electric current. Thus a solution of any salt of sodium is looked on as a solution of ions of sodium, that is, minute particles of sodium all carrying the same charge of positive electricity; in the case of sodium sulphate the theory regards the solution as also containing negatively charged ions of SO_4 , and a solution of sodium nitrate as containing negatively charged ions of NO_3 ; and so on.¹

Supposing, then, that aqueous solutions of two normal salts are mixed, the solution, according to this theory, will contain four kinds of ions, and the reactions of the solution will be the reactions of these ions; hence—to take an instance—the reactions

¹ This theory will be referred to more fully in an Appendix to Part II.

of a mixture of sodium chloride and magnesium nitrate in solution are the same as those of a mixture of solutions of sodium nitrate and magnesium chloride.

This theory at once explains why a solution of any salt of a certain metal gives the same reactions as a solution of any other salt of that metal so far as the metal is concerned: for instance, solutions of nitrate, chloride, sulphate, and acetate, of copper all give the same reactions so far as copper is concerned; because these solutions all contain ions of copper.

To take another instance: all ferric compounds in solution give a reddish pp. of ferric hydroxide (FeO_3H_3) with ammonia, and a black pp. of iron sulphide (FeS) with ammonium sulphide; now a solution of potassium ferrocyanide ($\text{K}_4\text{Fe}(\text{CN})_6$) gives no pp. with ammonia, nor does it give a pp. with ammonium sulphide; but iron is one of the components of this salt. The theory which explains the reactions of analytical chemistry as the reactions of ions is at once applicable to this case. This theory supposes that solutions of ferric compounds all contain the ion Fe , carrying three positive electric charges; but a solution of potassium ferrocyanide contains four potassium ions, each carrying a positive charge, and the ion $\text{Fe}(\text{CN})_6$ carrying four negative charges. Hence, as a solution of $\text{K}_4\text{Fe}(\text{CN})_6$ does not contain iron ions, it does not give the reactions of iron ions.

The electrolytic ionisation theory not only gives a general explanation of the facts of qualitative analysis, but it permits accurate statements to be made which contain the whole theory of analytical chemistry, and which can be applied directly, in a very detailed way, to the reactions and procedure of analysis.

The method that is most generally applicable for finding what radicles are present in a solution of a salt, or a mixture of salts, consists in adding reagents which react with the radicles present to produce substances that can be recognised by their characteristic properties. The substances thus produced are very often compounds which separate from the liquid wherein they are formed; these compounds are recognised by such properties as colour, appearance, solubilities in various reagents, and so on. For instance, an aqueous solution of any soluble salt of barium

reacts with a dilute solution of sulphuric acid to form barium sulphate, which is a heavy, white solid, insoluble in dilute solutions of acids, and which, therefore, is precipitated; in other words, the formation of a heavy, white precipitate, insoluble in dilute acids, when a little sulphuric acid is added to a solution of a salt, is a test for the presence of barium. Sometimes a gas is produced by a reaction between a reagent and the radicles in a solution of a salt, or a mixture of salts; and this gas is recognised by its smell or colour, or by its reactions with other reagents. For instance, an aqueous solution of a carbonate interacts with a dilute solution of any common acid to produce carbon dioxide, some of which is given off, and is recognisable by certain physical properties and by reacting with lime water to form chalk. Again, an aqueous solution containing a bromide and a bromate interacts with a few drops of a dilute solution of an acid to produce bromine, which is recognised by its smell, by the colour it imparts to the liquid, and by its ready solubility in carbon disulphide, which liquid it colours reddish.

It is often possible to use a characteristic property or reaction of the solid compounds of a metal, or the solid compounds of an acidic radicle, as a test to detect the metal, or the acidic radicle, in question. For instance, a deep blue, transparent, glass-like solid is obtained by heating a small quantity of a compound of cobalt mixed with a little borax, keeping the substance melted in the air for a short time, and then allowing it to cool. The formation of a deep blue glass, under these conditions, is a characteristic property of compounds of cobalt; and this reaction is used as a dry test for the detection of the metal cobalt. Again, when a small quantity of a silicate is fused with microcosmic salt (sodium-ammonium phosphate), a colourless, transparent glass is formed, wherein the little particles of silica may be seen floating about, undissolved, in the melted salt. This reaction is used as a test for the detection of the acidic radicle of the silicates. When a compound of strontium is volatilised in a non-luminous flame, the flame is coloured red; on this property of compounds of strontium is based a method for detecting strontium. If a compound of arsenic is supported in the slightly luminous tip of a small flame, a little arsenic is

formed and volatilised; the arsenic may be caught on the cold surface of a porcelain dish, and the blackish film so produced may be proved to be arsenic by the application to it of suitable reagents.

Some of the examples referred to in the two preceding paragraphs are illustrations of what are called *wet tests*, and others are illustrations of *dry tests*; the reactions used as tests in qualitative analysis fall, broadly, into these two classes.

In conducting wet tests, the substance to be examined is dissolved, and the solution is caused to interact with reagents that are themselves in solution. Dry tests consist in the application of solid reagents to the solid substance which is being examined; heat is generally employed to aid the reactions.

Reagents in solution are sometimes applied to a solid substance that is being analysed qualitatively; and a solution of the substance under examination is sometimes added to a solid reagent.

In the following experiments bearing on the classification of the reactions of qualitative analysis dry tests will be considered only incidentally.

For a systematic statement of dry tests, see Lesson LII.

Salts, using the term *salt* in a very wide sense, are regarded for the purposes of qualitative analysis as composed of metallic and acidic radicles. The metals are divided into groups, and the members of each group exhibit certain common reactions which distinguish them from the members of the other groups. The acidic radicles are also divided into groups; but the grouping is not carried out fully or consistently. We shall, therefore, begin with the metals.

LESSON XLI

EXPERIMENTS TO ILLUSTRATE THE METHODS USED FOR
DIVIDING THE METALS INTO GROUPS

Apparatus and materials required.—Apparatus to make hydrogen sulphide. Piece of clean platinum wire. The following salts: lead nitrate, silver nitrate, mercuric chloride, copper sulphate, copper nitrate, aluminium sulphate, zinc sulphate, calcium chloride, magnesium sulphate, potassium nitrate, sodium chloride. About half a dozen solutions, each containing a single salt; the salts being selected so that the metals of them belong to different groups.

NOTE.—It is assumed that each student is furnished with a set of apparatus comprising test-tubes, beakers, basins, funnels, filters, &c., and also with the ordinary reagents.

Experiment I.—*To illustrate the division of metals into groups.*

Pour into clean test-tubes such quantities of aqueous solutions of salts of about half a dozen metals, taken haphazard, as suffice to fill the tubes about one-tenth, and to each solution add about 20 drops of *dilute hydrochloric acid*; pps. will probably be produced in some of the solutions. Fill up those solutions wherein pps. have not been produced with an aqueous solution of *hydrogen sulphide*; pps. will probably be produced in some of the solutions. Assuming, what can be proved, that the pps. obtained are compounds of the metals of the salts used (with chlorine and sulphur, respectively), then, so far as the results of this experiment go, the metals examined may be divided into three groups:—(1) those which give pps. with hydrochloric acid; (2) those which do not give pps. with this acid, but are precipitated by hydrogen sulphide added to solu-

tions containing hydrochloric acid; and (3) those which are not precipitated either by hydrochloric acid, or by hydrogen sulphide added to solutions containing hydrochloric acid.

Experiment II.—*To illustrate the division of metals into groups.*

Dissolve about half a gram of each of the following salts in not more than one-fourth of a test-tubeful of water in a clean test-tube:—lead nitrate ($\text{Pb}(\text{NO}_3)_2$), mercuric chloride (HgCl_2), aluminium sulphate ($\text{Al}_2(\text{SO}_4)_3$), zinc sulphate (ZnSO_4), calcium chloride (CaCl_2), magnesium sulphate (MgSO_4), and sodium chloride (NaCl).

These solutions are regarded for the present purpose as solutions of the metals lead, mercury, aluminium, zinc, calcium, magnesium, and sodium; no attention is paid to the acidic radicles of the salts.

Set the test-tubes containing the solutions in a stand in the order given, and add to each a few drops of dilute hydrochloric acid. A white pp. of lead chloride (PbCl_2) forms in the solution containing lead; there is no visible change in the other solutions. To the solutions wherein pps. have not been produced add an aqueous solution of hydrogen sulphide, until the smell of this gas is distinctly perceptible. A black¹ pp. of mercuric sulphide (HgS) forms in the solution containing mercury; there is no visible change in the other solutions.

Place the solutions wherein pps. have not been produced in basins, and boil until every trace of hydrogen sulphide is removed;² then transfer the liquids to test-tubes, and add to each nearly quarter a test-tubeful of ammonium chloride solution, and then ammonia solution IN EXCESS, that is, until the smell of ammonia is perceptible after thoroughly mixing the contents of the tubes. A white gelatinous pp. (which is easily overlooked)

¹ Notice that the pp. formed at first is grey, then the pp. becomes orange, and finally black.

² Hydrogen sulphide is a gas; when a solution containing this gas is boiled the gas is driven out of the solution. The gas has been all expelled when the steam coming from the boiling liquid has not the slightest smell of hydrogen sulphide, and does not produce a blackish stain (of lead sulphide) on paper dipped in a solution of a lead salt and held in the steam.

of aluminium hydroxide (AlO_3H_3) forms in the solution containing aluminium; there is no visible change in the other solutions.

To the solutions wherein pps. have not been produced add a few drops of ammonium sulphide solution. A white pp. of zinc sulphide (ZnS) forms in the solution containing zinc (the pp. may appear yellowish as the liquid is slightly yellow); there is no visible change in the other solutions.

To the solutions wherein pps. have not been produced add about a sixth of a test-tubeful of ammonium carbonate solution. A white pp. of calcium carbonate (CaCO_3) forms in the solution containing calcium; there is no visible change in the other solutions.

To the solutions wherein pps. have not been produced add about a sixth of a test-tubeful of sodium phosphate solution, and shake vigorously. A white pp. of magnesium-ammonium phosphate (MgNH_4PO_4) forms slowly in the solution containing magnesium; there is no visible change in the solution containing sodium.

The formation of the foregoing pps. depends on the solubilities of the compounds produced in the reactions. When hydrochloric acid is added to solutions containing, respectively, lead, mercury, aluminium, zinc, calcium, magnesium, and sodium, lead is the only metal present that forms a compound insoluble in the liquid; this insoluble compound (lead chloride, PbCl_2) is, therefore, precipitated. When hydrogen sulphide is added to solutions containing hydrochloric acid and, respectively, mercury, aluminium, zinc, calcium, magnesium, and sodium, mercury is the only one of these metals that forms a compound insoluble in the liquid; this compound (mercuric sulphide, HgS) is, therefore, precipitated. When ammonia is added to solutions free from hydrogen sulphide and containing ammonium chloride and, respectively, aluminium, zinc, calcium, magnesium, and sodium, the only one of these metals that forms a compound insoluble in the liquid is aluminium; this compound (aluminium hydroxide, AlO_3H_3) is, therefore, precipitated. Similarly in the remaining cases: zinc sulphide is insoluble in a liquid containing ammonia and ammonium sulphide, but the sulphides of calcium, magnesium, and sodium are soluble in this liquid; calcium carbonate is insoluble, but magnesium carbonate and sodium carbonate are soluble, in an alkaline liquid containing ammonium carbonate and ammonium chloride; magnesium-ammonium phosphate is insoluble in an alkaline liquid containing ammonium chloride and sodium phosphate. None of the compounds of sodium formed by addition of the reagents mentioned to a solution containing sodium is insoluble in the liquids produced; sodium, therefore, is not precipitated by any of these reagents.

The foregoing experiment shows that certain metals may be distinguished from one another by the reactions of solutions containing these metals with reagents; the principle of the method being that one metal interacts with a certain reagent to produce a compound which is insoluble in the solution wherein it is formed, and which is, therefore, precipitated from this solution, while the compounds formed by the interactions of other metals with the same reagent are soluble in the solution, and, therefore, are not precipitated.

Each of the metals solutions of which have been used, in *Experiment II.* represents a group of metals. The metals in one group behave like lead: they all react, in solution, with dilute hydrochloric acid to form chlorides that are insoluble in dilute hydrochloric acid; these metals, therefore, are all precipitated by that reagent. The metals in another group behave like mercury: they all react, in solutions containing hydrochloric acid, with hydrogen sulphide to form sulphides that are insoluble in dilute hydrochloric acid and in hydrogen sulphide solution; these metals, therefore, are all precipitated by those reagents. The metals in another group behave like aluminium, and are precipitated by ammonia in presence of ammonium chloride. The metals of a fourth group behave like zinc; those of a fifth group, like calcium; and so on.

The reagents used in *Experiment II.* are called **group reagents**, because each of them precipitates a group of metals. The members of any group of metals have the common property of reacting, in solutions, with the group reagent to form compounds that are insoluble in that reagent, and, therefore, are precipitated by that reagent.

The results of *Experiment II.* show that the action of a group reagent is not interfered with by the presence of those group reagents that were added before it; in other words, the action of hydrogen sulphide is not interfered with by the presence of hydrochloric acid in the solution, nor is the action of ammonium carbonate interfered with by the presence of ammonium chloride, ammonia, and ammonium sulphide; and so on. *This holds good only if the group reagents are added in the order in which they are used in Experiment II.*

It should be noticed here that hydrogen sulphide was removed from the solution before the group reagents ammonium chloride and ammonia were added, in Experiment II.; if hydrogen sulphide had not been removed, this reagent would have interfered with the action of the ammonium chloride and ammonia, inasmuch as ammonium sulphide would have been formed by the reaction of hydrogen sulphide and ammonia, and this ammonium sulphide would have precipitated (as zinc sulphide) the zinc that was in the solution.

It is important for the student to understand clearly that it is necessary to use the group reagents in the order in which they were employed in *Experiment II.* The following experiment will enforce this necessity.

Experiment III.—*To illustrate the necessity of adding the group reagents in a definite order.*

Make a solution of about a gram of lead nitrate in about a test-tubeful of water, and divide the solution into five parts.

To one part of this solution add hydrogen sulphide solution (the reagent for *Group II.*); a black pp. (PbS) is formed, and this pp. does not dissolve when a little dilute hydrochloric acid is poured on to it.

To another part of the solution add ammonia (the reagent for *Group III.*); a white pp. (PbO_2H_2) forms.

To another part of the solution add ammonium sulphide (the reagent for *Group IV.*); a black pp. (PbS) is produced.

To another part of the solution add solution of ammonium carbonate (the reagent for *Group V.*); a white pp. (PbCO_3) appears.

To the last part of the solution of lead nitrate add solution of sodium phosphate (the reagent for *Group VI.*); a white pp. ($\text{Pb}_3\text{P}_2\text{O}_8$) settles down.

Lead, then, resembles mercury in that its sulphide is precipitated on addition of hydrogen sulphide; it resembles aluminium in giving a pp. of the hydroxide with ammonia; it resembles zinc in yielding a pp. of the sulphide with ammonium sulphide; it resembles calcium in that the carbonates of both these metals are precipitated on addition of ammonium carbonate; and it resembles magnesium in being thrown down as

phosphate by a solution of sodium phosphate. But *Experiment II.* showed that lead differs from all these metals in that it, and it alone, forms a chloride which is insoluble in dilute hydrochloric acid.

If hydrogen sulphide produces a pp. in a solution of a salt, it does not follow that the metal of this salt belongs to *Group II.*; but if addition of dilute hydrochloric acid does not form a pp., and if addition of hydrogen sulphide to this liquid, which now contains hydrochloric acid, does produce a pp., the metal of the salt is certainly a metal of *Group II.* Again, the formation of a pp. when ammonium carbonate is added to a solution of a salt does not prove the metal of the salt to be one of those comprised in *Group V.*; but if it is also found that the solution in question is not precipitated on addition of hydrochloric acid, followed by addition of hydrogen sulphide, followed by boiling off the hydrogen sulphide and then adding ammonium chloride and excess of ammonia, and then ammonium sulphide, the conclusion is inevitable that the metal belongs to *Group V.*

The following table shows (1) the group reagents, (2) the metals in each group, and (3) the compositions of the pps. produced by the group reagents.

Only the commoner metals are considered.

Group Reagents	Metals in the Group	Compositions of Pps. produced by Group Reagents
Group I. Dilute hydrochloric acid.	Lead; silver; mercurousum. The name <i>mercurousum</i> is given to mercury in mercurous salts to distinguish it from mercury in mercuric salts.	PbCl_2 ; AgCl ; HgCl .
Group II. Hydrogen sulphide, added to solutions containing a little hydrochloric acid.	Lead; mercurium; copper; cadmium; bismuth; arsenic; antimony; tin. The name <i>mercurium</i> is given to mercury in mercuric salts, to distinguish it from mercury in mercurous salts. As lead chloride is slightly soluble in dilute hydrochloric acid, lead cannot be precipitated completely in Group I.; lead, therefore, is placed in Groups I. and II.	PbS ; HgS ; CuS ; CdS ; Bi_2S_3 ; As_2S_3 ; Sb_2S_3 ; SnS and SnS_2 . Stannous salts give a pp. of SnS , and stannic salts a pp. of SnS_2 .

Group Reagents	Metals in the Group	Compositions of Pps. produced by Group Reagents
GROUP III. Ammonia, added to solutions containing ammonium chloride and free from hydrogen sulphide.	Iron; aluminium; chromium.	FeO_3H_2 ; AlO_3H_3 ; CrO_3H_3 .
GROUP IV. Ammonium sulphide, added to solutions containing ammonium chloride and ammonia.	Zinc; manganese; nickel; cobalt.	ZnS ; MnS ; NiS ; CoS .
GROUP V. Ammonium carbonate, added to solutions containing ammonium chloride and ammonia. The presence or absence of ammonium sulphide does not affect the reaction of the group reagent.	Calcium; barium; strontium.	CaCO_3 ; BaCO_3 ; SrCO_3 .
GROUP VI. Sodium phosphate, added to solutions containing ammonium chloride and ammonia. The presence or absence of ammonium sulphide and ammonium carbonate does not affect the action of the group reagent.	Magnesium.	$\text{MgNH}_4\text{PO}_4 \cdot x\text{H}_2\text{O}$.
GROUP VII. No group reagent. The metals in this group are not precipitated by any of the foregoing group reagents.	Sodium; potassium; ammonium.	

Experiment IV.—*To use the foregoing table for the purpose of determining to what group a metal belongs.*

Several solutions, each containing one of the metals mentioned in the table (the metal not being known), should be examined, and the group to which the metal belongs should be determined.

In conducting these determinations proceed as follows:—

Group I. Group reagent is *hydrochloric acid*.

Group II. Group reagent is *hydrogen sulphide added after hydrochloric acid*.

Group III. Group reagent is *ammonia added after ammonium chloride (hydrogen sulphide being absent.)*

Group IV. Group reagent is *ammonium sulphide added after ammonia*.

Group V. Group reagent is *ammonium carbonate added after ammonia*.

Group VI. Group reagent is *sodium*

- (i.) To about an eighth of a test-tubeful of the solution add about a dozen drops of dilute *hydrochloric acid*; if a pp. forms, the metal belongs to Group I.
 - (ii.) If hydrochloric acid does not produce a pp., to the same liquid add *hydrogen sulphide* till the liquid smells strongly of this gas; if a pp. forms, the metal belongs to Group II.
 - (iii.) If hydrogen sulphide does not produce a pp., to about an eighth of a test-tubeful of the original liquid add about an equal quantity of *ammonium chloride* solution, and then excess of *ammonia*; if a pp. forms, the metal belongs to Group III.
- NOTE.—Using the original liquid for (iii.) is equivalent to, and is done more easily than, boiling out the hydrogen sulphide that was added in (ii.); *Groups I. and II. have been proved absent.*
- (iv.) If ammonia does not produce a pp., to the same liquid add *five or six drops of ammonium sulphide*; if a pp. forms, the metal belongs to Group IV.
 - (v.) If ammonium sulphide does not produce a pp., to the same liquid add about quarter of a test-tubeful of *ammonium carbonate* solution and warm the liquid for a few minutes; if a pp. forms, the metal belongs to Group V.
 - (vi.) If ammonium carbonate does not produce a pp., to the same liquid

phosphate added
after ammonium
chloride and am-
monia.

Group VII. No group
reagent.

add about quarter a test-tubeful of sodium phosphate solution, and shake vigorously; if a pp. forms, the metal belongs to Group VI.

In this case the metal must be magnesium, as this is the only metal in Group VI.

(vii.) If sodium phosphate does not produce a pp., the metal belongs to Group VII.

Experiment V.—To illustrate the grouping of the metals, and the separation of group from group.

Make a mixture of small quantities of aqueous solutions of the following salts (about one-tenth of a test-tubeful of each solution should be used; the solutions should contain about one part of salt in 20 to 30 parts of water)—silver nitrate (AgNO_3), copper sulphate (CuSO_4), aluminium sulphate ($\text{Al}_2(\text{SO}_4)_3$), zinc sulphate (ZnSO_4), calcium nitrate ($\text{Ca}(\text{NO}_3)_2$), magnesium sulphate (MgSO_4), and potassium nitrate (KNO_3).

Group I.—To about quarter a test-tubeful of this mixture of solutions of these salts add a few drops of dilute hydrochloric acid, and shake thoroughly (dilute hydrochloric acid is generally prepared in the laboratory by adding about three parts of water to one part of the conc. acid); let the white pp. of silver chloride (AgCl) settle, and then pour the liquid through a filter, letting the filtrate run into a clean beaker.

The silver is thus removed from the solution.

Group II.—Warm the filtrate from the pp. of silver chloride, and pass hydrogen sulphide into it until the smell of hydrogen sulphide is very marked; then add a little water and warm, very gradually raising the temperature nearly but not quite to the boiling point; again pass hydrogen sulphide into this warm liquid for some minutes, allow to stand for fully five minutes, and then collect the black pp. of copper sulphide (CuS) on a filter, allowing the filtrate to run into a clean beaker.

The copper is thus removed from the solution.

NOTE.—Addition of a slight excess of any group reagent except hydrogen sulphide quickly precipitates all the metals of the group that may be

present in the solution; but a very large excess of hydrogen sulphide is needed to precipitate completely the metals of *Group II*. The precipitation by hydrogen sulphide is effected most rapidly and completely under the conditions described above.

Group III.—Add about one-tenth of a test-tubeful of dilute, *nitric acid* to the filtrate from the pp. of copper sulphide, and boil, in a basin, until there is not the slightest smell of hydrogen sulphide, and a piece of paper moistened with a solution of a salt of lead is not turned brown when held in the steam (see *Note*); then, but not till then, add to the solution a good deal (say quarter a test-tubeful) of *ammonium chloride* solution, and then excess of *ammonia* solution, (until the smell of ammonia is apparent after thoroughly mixing the liquid); filter off the white, gelatinous, almost transparent, pp. of aluminium hydroxide (AlO_3H_3), and collect the filtrate in a clean beaker.

The aluminium is thus removed from the solution; and the hydrogen sulphide which was present in the filtrate from the pp. of Group II. is also removed.

NOTE.—When a solution containing hydrogen sulphide is heated with nitric acid the hydrogen sulphide is oxidised to sulphurous and sulphuric acids, and some sulphur is also usually formed. The objects of heating the filtrate from the pp. of *Group II*. with nitric acid are (i.) to remove the whole of the hydrogen sulphide, and (ii.), if iron is present, to oxidise ferrous salts to ferric salts. Should iron be present in a solution, the filtrate from *Group II*. will contain a ferrous salt, as hydrogen sulphide reduces ferric to ferrous salts (see *Lesson XLV.*, *Experiment II.*).

Group IV.—To the filtrate from the pp. of aluminium hydroxide add a little *ammonium sulphide* (about a dozen drops), boil for some time, collect the white pp. of zinc sulphide (ZnS) on a filter, and let the filtrate run into a clean beaker.

The zinc is thus removed from the solution.

Group V.—To the filtrate from the pp. of zinc sulphide add a good deal (about quarter a test-tubeful) of *ammonium carbonate* solution, warm for some time (to complete the precipitation and to cause the pp. to settle), and collect the white pp. of calcium carbonate (CaCO_3) on a filter, and the filtrate in a clean beaker.

The calcium is thus removed from the solution.

Group VI.—To the filtrate from the pp. of calcium carbonate add about a fourth of a test-tubeful of *sodium phosphate* solu-

tion; shake thoroughly, allow to stand for a little time (precipitation is not completed at once), and filter off the white pp. of magnesium-ammonium phosphate (MgNH_4PO_4) that forms.

The magnesium is thus removed from the solution.

Group VII.—The last filtrate contains the potassium.

The results of *Experiment V.* may be tabulated thus:—

From a solution containing silver		
I. Hydrochloric acid precipitates silver chloride—	→ filtrate	copper
II. Hydrogen sulphide, in presence of hydrochloric acid, precipitates copper sulphide—	→ filtrate	aluminium
III. Ammonia, in presence of ammonium chloride and absence of hydrogen sulphide, precipitates aluminium hydroxide—	→ filtrate	zinc
IV. Ammonium sulphide, in presence of ammonium chloride and ammonia, precipitates zinc sulphide—	→ filtrate	calcium
V. Ammonium carbonate, in presence of ammonium chloride and ammonia, precipitates calcium carbonate—	→ filtrate	magnesium
VI. Sodium phosphate, in presence of ammonium chloride and ammonia, precipitates magnesium-ammonium phosphate—	→ filtrate	potassium
VII. Potassium remains in solution		

LESSON XLII

EXPERIMENTS TO ILLUSTRATE THE METHODS USED FOR
DISTINGUISHING THE SEVERAL METALS IN THE SAME
GROUP

Apparatus and materials required.—The following salts : lead nitrate, silver nitrate, mercurous nitrate, arsenious oxide, stannic chloride, cadmium nitrate or sulphate, bismuth nitrate, aluminium sulphate, ferric chloride, cobalt nitrate, nickel sulphate. Clean platinum wire. Apparatus to make hydrogen sulphide.

Experiment I.—*To illustrate the application of the colours and appearances of pps. to distinguish between metals belonging to the same group.*

The metals iron and aluminium belong to the same group (Group III.).

To small, separate, quantities¹ of solutions in water of ferric chloride and aluminium sulphate add about quarter a test-tubeful of ammonium chloride solution, and then excess of ammonia solution. Reddish brown, flocculent, ferric hydroxide (FeO_3H_3) is precipitated from the solution of ferric chloride; and white, gelatinous, opalescent, aluminium hydroxide (AlO_3H_3) is precipitated from the solution of aluminium sulphate.

Aluminium and iron (in ferric salts) are distinguished by the colour and appearance of the pps. produced by the group reagent (ammonia, in presence of ammonium chloride) from solutions of salts of these metals.

¹ In experiments of this kind use about a tenth of a test-tubeful of each solution, and let the solutions contain about one part of the salt in 20 to 30 parts of the solvent.

Experiment II.—*To illustrate the application of the solubilities of pps., and their behaviours towards reagents, to distinguish between metals belonging to the same group.*

Place in separate test-tubes small quantities of aqueous solutions of lead nitrate, silver nitrate, and mercurous nitrate, and to each add a few drops of *dilute hydrochloric acid*; a white, curdy pp. is produced in each case.

It is known (see *Table*, p. 228) that these pps. have the compositions PbCl_2 , AgCl , and HgCl , respectively.

The pps. are so similar in appearance that one cannot be distinguished clearly from the others.

Shake the tubes, and so cause the pps. to settle; pour off as much as possible of the liquids above the pps.; on to each pp. pour a *little* cold water, shake thoroughly, allow the pps. to settle, and pour away the supernatant liquids. Repeat this treatment with a *little* cold water. Now pour some *water* into each tube, and *boil*; the pp. of lead chloride gradually dissolves in the boiling water, but the other pps. do not dissolve.

Lead chloride is thus distinguished from silver chloride and from mercurous chloride by the fact that it is the only one of the three chlorides which dissolves in boiling water.

Now pour away the hot water from the pps. of silver chloride and mercurous chloride; add a little *ammonia* solution to each pp. and shake thoroughly; the silver chloride dissolves gradually, and the mercurous chloride is changed to a black solid.

Silver chloride and mercurous chloride are thus distinguished by the facts that the former dissolves gradually in ammonia solution, and the latter is converted by the same reagent into a black substance.

Experiment III.—*To illustrate the application of the solubilities of pps., and their behaviours towards reagents, to distinguish between metals belonging to the same group.*

The metals arsenic, cadmium, and tin belong to the same group (*Group II.*). Into small quantities of solutions, in *dilute* hydrochloric acid, of arsenious oxide and a salt of cadmium pass *hydrogen sulphide*, warm, and collect on filters the yellow

pps. that form. These pps. are arsenious sulphide (As_2S_3) and cadmium sulphide (CdS) respectively; both are light yellow, and they are too much alike to be distinguishable by their appearance. Wash the pps. once or twice with warm water, transfer portions of the pps. to test-tubes, add a little (say a tenth of a test-tubeful) ammonium sulphide solution, and warm for a few minutes; the pp. of arsenious sulphide dissolves, but the pp. of cadmium sulphide does not dissolve, in the warm solution of ammonium sulphide.

Arsenic is distinguished from cadmium by the facts, that arsenious sulphide, which is a yellow solid formed by passing hydrogen sulphide into a solution of a compound of arsenic containing a little hydrochloric acid, is soluble in warm ammonium sulphide, whereas cadmium sulphide, which is a yellow solid precipitated by hydrogen sulphide from an acidulated solution of a salt of cadmium, is insoluble in warm ammonium sulphide.

Now pass hydrogen sulphide into a warm solution of a little stannic chloride in dilute hydrochloric acid; a yellow pp. of stannic sulphide (SnS_2) is gradually formed. Heat to boiling (to cause the pp. to settle), collect the pp. on a filter, and wash it with warm water. Transfer two portions of the washed pp. to test-tubes; to one portion add a little ammonium sulphide solution, and warm; the pp. gradually dissolves.

So far as the experiment has proceeded, it has not furnished a means for distinguishing yellow stannic sulphide with certainty from yellow arsenious sulphide.

To the other portion of the pp. of stannic sulphide add some solid ammonium carbonate, and a little water, and warm; the pp. remains undissolved. Now precipitate a little arsenious sulphide (or use some of the arsenious sulphide precipitated in the earlier part of this experiment), and warm this pp. with some solid ammonium carbonate and a little water; the pp. gradually dissolves.

A stannic compound is distinguished from a compound of cadmium by the facts that yellow stannic sulphide is dissolved, whereas yellow cadmium sulphide is not dissolved, by warm ammonium sulphide.

And a stannic compound is distinguished from an arsenic compound by the facts that yellow stannic sulphide is not dissolved, whereas yellow arsenious sulphide is dissolved, by a warm concentrated solution of ammonium carbonate.

Experiment IV.—To illustrate the application of the solubilities of pps., and their behaviours towards reagents, to distinguish between metals belonging to the same group.

To small quantities of solutions,¹ in a very little *dilute nitric acid* (say one-twentieth of a test-tubeful), of a salt of bismuth and a salt of lead, add some water, and then pass in *hydrogen sulphide*; in each case a black, or very dark brown, pp. is formed. These pps. have the compositions Bi_2S_3 and PbS , respectively.

The two metals bismuth and lead belong to the same group (*Group II.*), and the pps. produced by the group reagent are too much alike to furnish a means of distinguishing the metals with certainty.

Wash the pps. as directed in *Experiment III.*, then to each pp. add a little moderately dilute *nitric acid* (about a twentieth of a test-tubeful of conc. acid diluted with its own bulk of water), and boil; both pps. dissolve gradually; in both cases a little hydrogen sulphide is given off during solution (detected by its smell), and some yellowish spongy solid is formed and floats about in the liquid (this solid is sulphur).

So far, the pps. of bismuth sulphide and lead sulphide have behaved very similarly.

Boil the solutions of the two precipitated sulphides in nitric acid for a few minutes (these solutions contain bismuth nitrate and lead nitrate, respectively), and filter if necessary; to the clear liquids add about a fourth of a test-tubeful of *dilute sulphuric acid*, and evaporate both liquids, in basins, to about half their original volumes; *allow to cool*, and then add a *little dilute sulphuric acid*. A white pp. will be seen to have formed in the solution that contained lead nitrate (this pp. is lead sulphate, PbSO_4); but no pp. will have formed in the solution that contained bismuth nitrate.

¹ See footnote to Experiment I. (p. 234).

- *Lead, then, resembles bismuth in that hydrogen sulphide produces black, or very dark brown, pps. from acidified solutions of these metals, which pps. are dissolved by heating with nitric acid. But lead is distinguished from bismuth by the facts that a solution containing lead gives a white pp. (PbSO_4) on evaporation with dilute sulphuric acid, whereas a solution containing bismuth does not give a pp. under similar conditions.*

Experiment V.—*To illustrate the application of the solubilities of pps., and their behaviours towards reagents, to distinguish between metals belonging to the same group.*

To small quantities of aqueous solutions of a salt of cobalt and a salt of nickel add about one-fourth of a test-tubeful of ammonium chloride solution, and then gradually add ammonia until there is an excess of this reagent; in each case a pp. is produced when a little ammonia is added, but both pps. dissolve when more ammonia solution is poured in. To these solutions now add a very few drops of ammonium sulphide solution, boil for some minutes, collect the black pps. of cobalt sulphide and nickel sulphide (CoS and NiS) on filters, and wash these pps. Remove portions of the black pps. to test-tubes, and shake them with very dilute hydrochloric acid, without warming; neither pp. dissolves. Pour off the liquids from above the pps., and to each pp. add a little concentrated hydrochloric acid, and two drops (not more) of nitric acid, and boil; both pps. gradually dissolve.

Cobalt and nickel, then, are both precipitated from alkaline solutions by ammonium sulphide; both pps. are black, and are insoluble in dilute, cold, hydrochloric acid, but are dissolved by hot conc. hydrochloric acid containing a very little nitric acid.

Now take two pieces of clean platinum wire, and make a small loop on the end of each; heat these loops, and dip them into powdered borax (sodium borate, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$); then heat the ends of the wires with the adhering borax in the flame of a Bunsen lamp until the borax melts, and becomes clear, colourless, glass-like beads. Bring a very little of the pp. of

cobalt sulphide on to one of the *borax beads*, and a very little of the nickel sulphide on to the other borax bead, and heat the beads in a Bunsen flame until they are melted; then examine their appearances. The bead into which the cobalt sulphide has been melted is deep blue, and the bead into which the nickel sulphide has been melted is reddish brown.

Cobalt is distinguished from nickel by the facts that cobalt sulphide (and other solid compounds of cobalt) reacts with melted borax to form a blue solid, and the solid formed by the reaction of nickel sulphide (and other solid compounds of nickel) with melted borax is reddish brown.

Experiments I. to V. illustrate the methods that are used in qualitative analysis for distinguishing from one another metals which are precipitated by the same group reagent.

Sometimes the colours and appearances of the pps. produced by the group reagent suffice to distinguish one metal from another of the same group; for instance, iron is distinguished from aluminium by differences between the appearances of the group pps. (FeO_3H_3 and AlO_3H_3) [*Experiment I.*, p. 284].

The colours and appearances of the pps. produced by the group reagent are often very similar: in such cases the solubilities of these pps. sometimes serve to distinguish one from others; for instance, all the pps. produced by the group reagent hydrochloric acid are white and very alike in appearance, but the only one of these white pps. (PbCl_2 , AgCl , and HgCl_2) which is soluble in hot water is lead chloride [*Experiment II.*]; again, the only one of the three yellow pps. (CdS , As_2S_3 , SnS_2) produced in *Group II.* which is insoluble in hot ammonium sulphide is cadmium sulphide [*Experiment III.*, p. 236].

Similar pps. in the same group are sometimes differentiated by the reactions of these pps. with a reagent; for example, mercurous chloride is the only one of the three white pps. of *Group I.* which interacts with ammonia to form a black compound [*Experiment II.*, p. 235].

There may be several pps. in the same group like one another, and all dissolving in the same reagent; in such cases reactions of

solutions of these pps. with a reagent, or with different reagents, often serve to identify the different metals; for example, the two dark-coloured pps. bismuth sulphide and lead sulphide, both formed in *Group II.*, dissolve in hot nitric acid, and the solution of lead nitrate thus produced gives a white pp. (PbSO_4) on addition of dilute sulphuric acid and evaporation, whereas this treatment does not cause the formation of a pp. in the solution of bismuth nitrate [*Experiment IV.*, p. 237].

The application of a dry test—frequently the reaction with melted borax—is sometimes the quickest and most conclusive way of differentiating two pps. which are very similar; for example, black cobalt sulphide dissolves in melted borax to form a blue compound, whereas black nickel sulphide dissolves in the same reagent to form a reddish brown compound [*Experiment V.*, p. 239].

The results of *Experiments I. to V.* may be summarised by saying that pps. containing metals of the same group are distinguished: (1) by their colours and appearances; (2) by some property of the pps., very frequently their solubilities or insolubilities in a reagent, or their reactions with a reagent; (3) by the reactions of solutions of these pps.

In every case the tests that are used must suffice to identify the metal without doubt; sometimes a single test suffices, but more often it is necessary to employ several *confirmatory tests*.

The reactions which serve to identify a metal occur under definite conditions; these reactions must, therefore, be used as tests under definite conditions. For instance, the statement that a solution of a compound of iron gives a pp. with an excess of ammonia, is not sufficiently exact to serve as the basis of a test for iron; but the statement that a solution of a ferric compound, free from compounds of other metals, gives a reddish brown pp. of ferric hydroxide when excess of ammonia is added, is sufficiently exact to serve as the basis of a test for iron. Again, if a pp. is produced by passing hydrogen sulphide into a solution, the conclusion cannot be drawn that a metal (or metals) of *Group II.* is present in the solution, because the metals of *Group I.* are precipitated by hydrogen sulphide from an acid or

an alkaline solution, and the metals of *Groups III. and IV.* are precipitated by the same reagent from alkaline solutions. But if it is known that none of the metals of *Group I.* is present in a solution, and if, after making that solution slightly acid by hydrochloric acid, hydrogen sulphide produces a pp., then it follows that the solution contains a metal, or metals, of *Group II.*

A reaction which proceeds very slowly, or is decidedly modified by small changes in such conditions as temperature, or quantity of water, or other reagent, present, cannot be employed as a qualitative test. For instance, addition of a solution of potassium iodide to a cold, fairly concentrated, solution of a salt of bismuth in a very little acid, produces a brown pp. of bismuth iodide (BiI_3); but addition of the same reagent to a hot, somewhat dilute, solution of a salt of bismuth, precipitates red bismuth oxyiodide (BiOI). Solution of potassium iodide is not, therefore, a suitable reagent for detecting bismuth.

A consideration of the reactions used in the qualitative detection of metals, as illustrated by the foregoing experiments, will show that most of the tests are based on reactions between acids and salts, alkalis and salts, or salts and salts. For instance, the group reactions of *Groups I. and II.* consist in interactions of acids (hydrochloric and sulphydric acids) and salts of the metals of these groups, resulting in the formation of new salts which precipitate (chlorides in *Group I.* and sulphides in *Group II.*), and new acids which remain in solution. The group reaction of *Group III.* is an interaction of salts (of the metals of the group) and an alkali (ammonia), resulting in the formation of metallic hydroxides which are precipitated, and salts of the metal of the alkali (salts of ammonium) which go into solution. The group reactions of *Groups IV. and V.* are interactions between salts (ammonium sulphide in *Group IV.* and ammonium carbonate in *Group V.*) and salts (of the metals of the groups), producing new salts which precipitate (sulphides of the metals of *Group IV.* and carbonates of the metals of *Group V.*), and other new salts (of ammonium which go into

GENERAL REMARKS ON THE APPLICATION OF
THE TWO FOREGOING LESSONS

The application of the reactions of the kind illustrated in the preceding paragraphs to the qualitative analysis of a mixture of metals must proceed in a systematic manner. The plan followed is first to find reactions each of which is common to several metals, and by using these common reactions to divide the metals into groups; then to find a reaction peculiar to one metal, whereby that metal may be separated from the other members of its own group; and, finally, to identify the metal thus separated by applying a reaction which is characteristic of that metal. The second and third stages are sometimes combined into one, by using a reaction which at once separates a certain metal from the other members of its group, and also identifies the metal thus separated. In some cases it is not necessary to separate a metal from other metals belonging to the same group in order to identify the metal in question: for instance, addition of excess of ammonia to a solution containing copper and any, or all, of the other metals of *Group II.*, produces an azure-blue liquid; as the colour of the liquid is visible even if the liquid contains pps. produced by the ammonia, this reaction of compounds of copper may be applied to detect copper in a solution containing all the metals of the second group.

The formation of a satisfactory plan for the qualitative analysis of a mixture of all the common metals requires an exhaustive study of the reactions of these metals, and of some of the physical properties of their compounds, and the selection of those reactions and properties which are most suitable for the purpose of dividing the metals into groups, and of those reactions and properties which serve best for the identification of each member of each group.

It would be absurd to require every student of qualitative analysis to make such an exhaustive, and exhausting, study as this. The learner must use the experience of those who have gone before him, and be content to restrict himself to certain selected reactions, and to use the plan of analysis that has been found to work satisfactorily.

The immediate object at present is to become acquainted with the methods employed for detecting the metals in a mixture of salts, or in a mixture of metals, arranged so that not more than a single metal is present in the same group. For this purpose it will be sufficient for the student to perform the experiments on the reactions that are used for detecting a metal of each group; then to examine the synopses of those reactions; then to detect one metal in *Group I.*, then one metal in *Group II.*, and generally one metal in a group when the group is known; and finally, to detect the metals in a mixture which may contain a single metal in each group.

LESSON XLIII

DETECTION OF A SINGLE METAL KNOWN TO BELONG TO GROUP I

Materials required.—Solution of a salt of lead, a salt of silver, and a mercurous salt. A few salts of these metals in solution, and a few solid salts.

The metals in this group are *silver, mercurous, and lead.*

Group reagent is a dilute solution of hydrochloric acid.

The pps. produced by the group reagent are AgCl , HgCl , and PbCl_2 ; these pps. are white.

Experiment I.—*To become acquainted with the reactions used for detecting a metal of Group I.*

To small quantities (about a tenth of a test-tubeful) of solutions of lead nitrate, silver nitrate, and mercurous nitrate add a few drops of dilute *hydrochloric acid*; shake the tubes thoroughly; let the pps. settle, and then pour off the supernatant liquids; add a *very little* distilled water to each pp., shake, let pps. settle, and pour off the liquids; repeat this washing process. Add about quarter a test-tubeful of *distilled water* to each washed pp. and boil for a few minutes. The lead chloride dissolves, but both the silver chloride and the mercurous chloride remain unchanged. To the solution of lead chloride in hot water add solution of *potassium chromate*; a yellow pp. of lead chromate is produced. Add *acetic acid* to this pp.; the pp. does not dissolve.

Pour off the warm water from above the pps. of silver chloride and mercurous chloride; to each pp. add about a tenth of a test-tubeful of *ammonia* solution, and shake. The pp. of silver chloride dissolves; and the pp. of mercurous chloride is changed to a black substance. To the solution of silver chloride in ammonia add *nitric acid* solution till the liquid is acid; a white pp. of silver chloride is produced.

Pour off the ammonia solution from above the black substance

produced by shaking the pp. of mercurous chloride with ammonia; add about 20 drops of *conc. hydrochloric acid* and about 10 drops of *conc. nitric acid* to the black solid and boil. The black solid dissolves; to the solution add *stannous chloride* solution, drop by drop; a white pp. of mercurous chloride is produced; and after a moderate quantity of stannous chloride has been added this white pp. changes to a black solid which is mercury.

Synopsis of those Reactions of the Metals of Group I. which are Employed in Detecting One of these Metals.

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|---|---|--|
| The white
pp. pro-
duced by
hydro-
chloric
acid is | { | (1) Soluble in <i>hot water</i> = PbCl_2 ; the solution in hot water gives a yellow pp. (PbCrO_4) with <i>potassium chromate</i> , which pp. is insoluble in <i>acetic acid</i> .
(2) Insoluble in <i>hot water</i> = AgCl or HgCl .
(8) Insoluble in <i>hot water</i> ,
and soluble in <i>ammonia</i> = AgCl ; the solution in ammonia gives a white pp. of AgCl with excess of <i>nitric acid</i> (AgCl in $\text{NH}_3\text{Aq} + \text{HNO}_3\text{Aq} = \text{NH}_4\text{NO}_3\text{Aq} + \text{AgCl}$).
(4) Insoluble in <i>hot water</i> ,
and blackened by <i>ammonia</i> = HgCl ; the black compound ($\text{NH}_2\text{Hg}_2\text{Cl}$) dissolves in hot <i>aqua regia</i> , and this solution, which contains HgCl_2 , gives a grey-black pp. (HgCl and Hg) with <i>stannous chloride</i> .
[(1) $2\text{HgCl}_2\text{Aq} + \text{SnCl}_2\text{Aq} = 2\text{HgCl} + \text{SnCl}_4\text{Aq}$; (2) $2\text{HgCl} + \text{SnCl}_2\text{Aq} = 2\text{Hg} + \text{SnCl}_4\text{Aq}$.] |
|---|---|--|

Experiment II.—To apply the results of *Experiment I.* to find out what metal is present in a salt which is known to be a salt of lead, silver, or mercurous; or to find out which of these three metals is the metal given you.

A. If the salt or metal is given in solution proceed as follows. If the substance is a solid see **B** (p. 246).

To about one-tenth of a test-tubeful of the solution add *dilute hydrochloric acid* until there is a slight excess of acid.

LESSON XLIII

DETECTION OF A SINGLE METAL KNOWN TO BELONG TO GROUP I

Materials required.—Solution of a salt of lead, a salt of silver, and a mercurous salt. A few salts of these metals in solution, and a few solid salts.

The metals in this group are *silver, mercurousum, and lead.*

Group reagent is a dilute solution of hydrochloric acid.

The pps. produced by the group reagent are AgCl , HgCl , and PbCl_2 ; these pps. are white.

Experiment I.—*To become acquainted with the reactions used for detecting a metal of Group I.*

To small quantities (about a tenth of a test-tubeful) of solutions of lead nitrate, silver nitrate, and mercurous nitrate add a few drops of dilute *hydrochloric acid*; shake the tubes thoroughly; let the pps. settle, and then pour off the supernatant liquids; add a *very little* distilled water to each pp., shake, let pps. settle, and pour off the liquids; repeat this washing process. Add about quarter a test-tubeful of *distilled water* to each washed pp. and boil for a few minutes. The lead chloride dissolves, but both the silver chloride and the mercurous chloride remain unchanged. To the solution of lead chloride in hot water add solution of *potassium chromate*; a yellow pp. of lead chromate is produced. Add *acetic acid* to this pp.; the pp. does not dissolve.

Pour off the warm water from above the pps. of silver chloride and mercurous chloride; to each pp. add about a tenth of a test-tubeful of *ammonia* solution, and shake. The pp. of silver chloride dissolves; and the pp. of mercurous chloride is changed to a black substance. To the solution of silver chloride in ammonia add *nitric acid* solution till the liquid is acid; a white pp. of silver chloride is produced.

Pour off the ammonia solution from above the black substance

produced by shaking the pp. of mercurous chloride with ammonia; add about 20 drops of *conc. hydrochloric acid* and about 10 drops of *conc. nitric acid* to the black solid and boil. The black solid dissolves; to the solution add *stannous chloride* solution, drop by drop; a white pp. of mercurous chloride is produced; and after a moderate quantity of stannous chloride has been added this white pp. changes to a black solid which is mercury.

Synopsis of those Reactions of the Metals of Group I. which are Employed in Detecting One of these Metals.

- | | | |
|---|---|---|
| The white
pp. pro-
duced by
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acid is | { | (1) Soluble in <i>hot water</i> = PbCl_2 ; the solution in <i>hot water</i> gives a yellow pp. (PbCrO_4) with <i>potassium chromate</i> , which pp. is insoluble in <i>acetic acid</i> . |
| | | (2) Insoluble in <i>hot water</i> = AgCl or HgCl . |
| | | (3) Insoluble in <i>hot water</i> ,
and soluble in <i>ammonia</i> = AgCl ; the solution in ammonia gives a white pp. of AgCl with excess of <i>nitric acid</i> (AgCl in $x\text{NH}_3\text{Aq} + \text{HNO}_3\text{Aq} = \text{NH}_4\text{NO}_3\text{Aq} + \text{AgCl}$). |
| | | (4) Insoluble in <i>hot water</i> ,
and blackened by <i>ammonia</i> = HgCl ; the black compound ($\text{NH}_2\text{Hg}_2\text{Cl}$) dissolves in <i>hot aqua regia</i> , and this solution, which contains HgCl_2 , gives a grey-black pp. (HgCl and Hg) with <i>stannous chloride</i> .
[(1) $2\text{HgCl}_2\text{Aq} + \text{SnCl}_2\text{Aq} = 2\text{HgCl} + \text{SnCl}_4\text{Aq}$; (2) $2\text{HgCl} + \text{SnCl}_2\text{Aq} = 2\text{Hg} + \text{SnCl}_4\text{Aq}$.] |

Experiment II.—To apply the results of Experiment I. to find out what metal is present in a salt which is known to be a salt of lead, silver, or mercurous; or to find out which of these three metals is the metal given you.

A. If the salt or metal is given in solution proceed as follows. If the substance is a solid see **B** (p. 246).

To about one-tenth of a test-tubeful of the solution add *dilute hydrochloric acid* until there is a slight excess of acid.

Collect the pp. on a filter.

Wash the pp. three or four times with cold water, *using a very little water each time.*

Transfer the washed pp. to a test-tube, and fill the tube nearly to one-half with *distilled water*, and boil for a few minutes :

(1) *The pp. dissolves in hot water ; the pp. was PbCl_2 , and, therefore, LEAD is present.*

Confirm this result by adding *potassium chromate* solution, and then *acetic acid*, to the solution in hot water of the pp. produced by hydrochloric acid; a yellow pp. is PbCrO_4 .

(2) *The pp. does not dissolve in hot water ; the pp. is AgCl or HgCl , and, therefore, either silver or mercurousum is present.*

To determine whether silver or mercurousum is present, let the pp. settle after boiling with water, pour off the hot water, add about quarter a test-tubeful of *ammonia* solution to the pp. and shake :

(a) *The pp. dissolves in ammonia ; to this solution add an excess of dilute nitric acid ; if a pp. forms which at first is white, but which turns violet when exposed to light, this pp. is AgCl , and, therefore, SILVER is present.*

(b) *The pp. is blackened by ammonia ; the pp. was HgCl , and, therefore, MERCUROSUM is present.*

Confirm this result by dissolving the black substance ($\text{NH}_2\text{Hg}_2\text{Cl}$) in a *very little hot aqua regia*, and adding *stannous chloride* to this solution, when a grey-black pp. of HgCl and Hg will be formed.

B. If the salt or the metal is a solid proceed as follows.

Place a *very little* of the substance in a test-tube, fill the tube to about one-fourth with *water* and boil. If all dissolves add a *little more* of the substance, boil till dissolved, and use this solution as directed under **A** (p. 245).

If the substance does not dissolve in water, boil a *little* of it with about quarter a test-tubeful of *dilute nitric acid* until it is dissolved, and use this solution as directed under **A** (p. 245).

LESSON XLIV

DETECTION OF A SINGLE METAL KNOWN TO BELONG TO
GROUP II

Materials required.—Solutions of a salt of each of the following metals; lead, copper, bismuth, cadmium, arsenic, antimony, and tin. A few salts of these metals in solution, and a few solid salts; also two or three of the metals themselves.

The metals in this group are *mercuricum, lead, copper, cadmium, bismuth, arsenic, antimony, and tin*. Lead is placed here as well as in Group I, because, as PbCl_2 is slightly soluble in dilute hydrochloric acid, this metal is not completely precipitated in Group I.

Group reagent is hydrogen sulphide passed into a solution containing hydrochloric acid.

The pps. produced by the group reagent are HgS , PbS , CuS , CdS , Bi_2S_3 , As_2S_3 , Sb_2S_3 , SnS from stannous compounds, and SnS_2 from stannic compounds; these pps. vary in colour from yellow to black.

Experiment I.—*To become acquainted with the reactions used for detecting a metal of Group II.*

To small quantities (about a tenth of a test-tubeful) of solutions of salts of the following metals, arranged in test-tubes in the following order—antimony, arsenic, stannic tin, cadmium, stannous tin, lead, bismuth, copper, mercuric mercury—add a few drops of dilute hydrochloric acid, and then fill up the tubes with a freshly prepared solution of hydrogen sulphide. Heat each liquid to boiling, put the test-tubes into the stand in the same order as before, and let the pps. settle: pour off the supernatant liquids; add a little water to each pp. and heat to boiling; let the pps. settle, and pour off the liquids from above the pps.

Transfer a small portion of the washed orange-red pp. of antimony sulphide to another test-tube, add a very little ammonium sulphide solution, and heat; the orange-red pp. of antimony sulphide dissolves. To this solution add hydrochloric acid in excess; orange-red Sb_2S_3 is re-precipitated.

Transfer *small portions* of the washed yellow pps. of arsenic sulphide, stannic sulphide, and cadmium sulphide to other test-tubes, add to each pp. a little *ammonium sulphide* solution, and heat; the yellow pps. of arsenic sulphide and stannic sulphide dissolve, while the yellow pp. of cadmium sulphide does not dissolve.

Transfer other *small portions* of the washed yellow pps. of arsenic sulphide and stannic sulphide to other test-tubes, add to each pp. a little solid *ammonium carbonate* and a *very little water*, and warm; the yellow As_2S_3 dissolves, while the yellow SnS_2 does not dissolve. To the solution of arsenic sulphide in ammonium carbonate solution add dilute *hydrochloric acid* till the liquid is acid; yellow As_2S_3 is re-precipitated. To the remainder of the washed yellow pp. of stannic sulphide add a *very little conc. hydrochloric acid*, and boil for a few minutes; the SnS_2 dissolves; pour the solution, which contains stannic chloride, into a basin, add some *copper turnings*, and a little water, and boil for *at least five minutes*; now pour off the liquid into a test-tube, and add to it a *very little mercuric chloride* solution; a pp. is produced which may be white (HgCl), or grey (HgCl mixed with Hg), or nearly black (Hg).

To the washed dark brown pp. of stannous sulphide add a little *ammonium sulphide* solution, and warm; the pp. dissolves; to this solution add dilute *hydrochloric acid* till the liquid is acid; yellow stannic sulphide (SnS_2) is precipitated.

Transfer *small portions* of the washed black pps. of sulphides of lead, bismuth, copper, and mercury, to other test-tubes, add to each a little *ammonium sulphide* solution, and warm; none of the pps. dissolves.

Transfer other *small portions* of the four washed black pps. to other tubes, add a little *nitric acid* (about one part conc. acid to three parts water) to each pp., and boil; the pps. of PbS , Bi_2S_3 , and CuS dissolve, but the pp. of HgS does not dissolve. Boil the solutions of the sulphides of lead, bismuth, and copper, in nitric acid for a few minutes (these solutions now contain nitrates of the metals), then add to each solution a little *dilute sulphuric acid* and boil for a short time; a white pp. (PbSO_4) forms in the tube which contained the solution of lead nitrate, but the two other solutions remain free from pps. To these two

solutions now add *ammonia in excess*: a white, gelatinous, pp. (BiO_3H_3) forms in the tube that contained the solution of bismuth nitrate, and an azure, blue colour is produced in the liquid which contained copper nitrate (this colour is due to the formation, in the solution, of $\text{CuO}_2\text{H}_2 \cdot 2\text{NH}_3$). Collect the white gelatinous pp. of BiO_3H_3 on a filter and wash it twice with warm water; then put a clean tube under the funnel, and pour *not more than a dozen drops* of hot dilute *hydrochloric acid* over the pp.; pour the solution (which contains bismuth chloride) into about three test-tubesful of water; a white pp. of BiOCl is produced.

To the black pp. of HgS which has not dissolved in boiling nitric acid add about ten drops of *conc. hydrochloric acid*, and boil; the pp. dissolves in the mixture of nitric and hydrochloric acids; to this solution, which contains HgCl_2 , add a few drops of *stannous chloride* solution; a grey pp. (Hg and HgCl) is produced.

Synopsis of those Reactions of the Metals of Group II. which are Employed in Detecting One of these Metals.

I. The pp. produced by hydrogen sulphide is yellow, and is

- (1) Insoluble in warm *ammonium sulphide* = CdS .
- (2) Soluble in warm *ammonium sulphide* = SnS_2 , or As_2S_3 (solution contains thio-stannates or thio-arsenites of ammonium).
- (8) Soluble in warm *ammonium sulphide*, also soluble in *conc. warm ammonium carbonate* solution = As_2S_3 ; *hydrochloric acid* re-precipitates As_2S_3 from the solution (of ammonium thio-arsenites) in ammonium carbonate.
- (4) Soluble in warm *ammonium sulphide*, but insoluble in warm *conc. ammonium carbonate* solution = SnS_2 ; this pp. dissolves in boiling *conc. hydrochloric acid* ($\text{SnS}_2 + 4\text{HClAq} = \text{SnCl}_4\text{Aq} + 2\text{H}_2\text{S}$); and when this solution is boiled with *copper*, stannous chloride is gradually formed ($\text{SnCl}_4\text{Aq} + \text{Cu} = \text{SnCl}_2\text{Aq} + \text{CuCl}_2\text{Aq}$); addition of *mercuric chloride* solution now produces a white pp. of HgCl , or a greyish pp. of HgCl mixed with Hg .

II. The pp. produced by hydrogen sulphide is *orange-red*, and is dissolved by warm *ammonium sulphide* = Sb_2S_3 ; *hydrochloric acid* re-precipitates Sb_2S_3 from the solution (of thio-antimonites) in ammonium sulphide.

III. The pp. produced by hydrogen sulphide is *black or dark-brown*, and is

- (1) Soluble in warm *ammonium sulphide* = SnS ; *hydrochloric acid* precipitates *yellow* SnS_2 from the solution of SnS , in *ammonium sulphide* (which solution contains $(\text{NH}_4)_2\text{SnS}_3$).
- (2) Insoluble in warm *ammonium sulphide* = HgS , PbS , CuS , or Bi_2S_3 .
- (3) Insoluble in warm *ammonium sulphide*, and also insoluble in hot *nitric acid* = HgS ; this pp. dissolves in warm *aqua regia*, and addition of *stannous chloride* to this solution, which contains HgCl_2 , forms a grey-black pp. (HgCl and Hg).
- (4) Insoluble in warm *ammonium sulphide*, but dissolved by hot *nitric acid* = PbS , CuS , or Bi_2S_3 .

The solution of this pp. in nitric acid contains $\text{Pb}(\text{NO}_3)_2$, $\text{Cu}(\text{NO}_3)_2$, or $\text{Bi}(\text{NO}_3)_3$, and gives

- (i.) a white pp. on adding a little *sulphuric acid* and evaporating; pp. = PbSO_4 ;
- (ii.) no pp. on evaporating with sulphuric acid, but a deep blue colour with *excess of ammonia*; colour due to formation in solution of $\text{CuO}_2\text{H}_2 \cdot 2\text{NH}_3$;
- (iii.) no pp. on evaporating with sulphuric acid, but a white gelatinous pp. with *excess of ammonia*; pp. is $\text{Bi}_2\text{O}_3 \cdot x\text{H}_2\text{O}$. This pp. dissolves in a little warm HClAq , and when the solution is poured into *much water* a white pp. of BiOCl is produced.

Before proceeding to make use of the reactions examined in *Experiment I.*, and tabulated in the synopsis of reactions, it is advisable to become acquainted with the conditions under which the precipitation of the metals of *Group II.* is effected success-

fully. For this purpose the two following experiments should be performed.

Experiment II.—*To become acquainted with the conditions under which the complete precipitation of the metals of Group II. is best effected.*

A. Pass *hydrogen sulphide* into moderately concentrated nitric acid (about equal parts conc. acid and water); a yellowish white, very finely divided, solid forms in the liquid. Pour the liquid through a filter; the filtrate is not clear, but still contains suspended solid matter. Continue to pass hydrogen sulphide into the nitric acid solution, then heat the liquid; there is a sudden deposition of finely divided yellow sulphur, the smell of nitrogen dioxide is apparent, but the liquid does not smell of hydrogen sulphide. Nitric acid and hydrogen sulphide interact, more quickly when heated, to form nitrogen dioxide, water, and sulphur; part of the sulphur may be oxidised, by oxygen from the nitric acid, to sulphurous and sulphuric acids, but some of it remains suspended in the liquid.

Now dissolve a little (say quarter a gram) cadmium nitrate or cadmium sulphate ($\text{Cd}(\text{NO}_3)_2$ or CdSO_4) in moderately dilute nitric acid (about one part conc. acid to three parts water), and pass *hydrogen sulphide* into this solution, warming after a time; no pp. except finely divided sulphur is produced until a very large quantity of the gas has been passed into the liquid, and the liquid has been very considerably diluted with water.

Finally, precipitate a little cadmium sulphide by adding *hydrogen sulphide* to a solution of a salt of cadmium in a *little very dilute hydrochloric acid*, and warming; wash the pp. two or three times with water, transfer it to a test-tube, add a few drops of moderately conc. nitric acid solution (about equal parts conc. acid and water), and warm; the cadmium sulphide dissolves.

The non-formation of cadmium sulphide by passing hydrogen sulphide into a solution of a salt of cadmium in moderately concentrated nitric acid solution is now accounted for; it has been shown (1) that nitric acid and hydrogen sulphide interact with the decomposition of both compounds, and (2) that cadmium sulphide dissolves in warm nitric acid solution.

The results of this part of Experiment II. make it evident

that nitric acid should not be present in a solution from which the metals of Group II. are to be precipitated by hydrogen sulphide.

B. Make a solution of about quarter a gram of a salt of cadmium in hydrochloric acid (equal parts conc. acid and water) and pass *hydrogen sulphide* into this solution for some time; the only pp. that forms is white finely divided sulphur. Now dilute the liquid with about its own bulk of water, and warm; a yellow pp. of cadmium sulphide (CdS) forms. Pass in more hydrogen sulphide, filter, dilute the filtrate, and warm; more yellow cadmium sulphide is precipitated. Again filter, add hydrogen sulphide to the filtrate, dilute, and warm; a further precipitation of yellow cadmium sulphide occurs. By repeatedly filtering, diluting, saturating with hydrogen sulphide, and warming, the whole of the cadmium in the solution will be precipitated as sulphide.

Pour off the liquid from the precipitated cadmium sulphide, add a little *dilute hydrochloric acid* to the pp., and warm; the cadmium sulphide does not dissolve. Now pour off the liquid from the pp., add some moderately concentrated hydrochloric acid (about equal parts conc. acid and water), and warm gently; the cadmium sulphide dissolves.

The results of Experiment II. show that the solution from which the metals of Group II. are to be precipitated by hydrogen sulphide should contain a little, but only a little, hydrochloric acid; that the liquid should be free from nitric acid; and that the liquid should be thoroughly saturated with hydrogen sulphide, then warmed, diluted somewhat, again saturated with the group reagent, and allowed to stand for a little time, to ensure the complete precipitation of the sulphides of the metals of this group.

Experiment III.—*The object of this experiment is to emphasise the need of adding a large excess of hydrogen sulphide to complete the precipitation of the sulphides of the metals of Group II.*

Dissolve about equal, small, quantities (say quarter a gram) of mercuric chloride and cadmium nitrate or sulphate in water, mix the solutions, and add a *very little dilute hydrochloric acid*, warm gently, and pass *hydrogen sulphide* into the solution until

the pp. is quite black and the liquid smells of hydrogen sulphide; now warm for a few minutes, and filter. Add some water to the filtrate, and pass hydrogen sulphide into it; a yellow pp. of cadmium sulphide is obtained, and no black pp. is produced even when the liquid is thoroughly saturated with hydrogen sulphide, and is then allowed to stand.

Knowing that mercuric sulphide is black, and cadmium sulphide is yellow, this experiment shows that it is possible to precipitate, by hydrogen sulphide, all the mercury from a slightly acidulated solution containing mercury and cadmium, and to leave some of the cadmium unprecipitated.

The first portion of the pp. produced by hydrogen sulphide in an acidulated solution of the metals of Group II. does not necessarily contain all the sulphides of the metals of the group; a greater excess of hydrogen sulphide, and a longer time, are required to precipitate cadmium sulphide completely than to complete the precipitation of mercuric sulphide.

Experiment IV.—*To apply the results of the foregoing experiments to find out what metal is present in a salt which is known to be a salt of mercuric mercury, lead, copper, cadmium, bismuth, arsenic, antimony, or tin; or to find out which of these metals is the metal given you.*

A. If the salt or metal is given in solution proceed as follows. If the substance is a solid see **B** (p. 256).

Add a few drops of dilute hydrochloric acid; then saturate about a quarter of a test-tubeful of the solution with hydrogen sulphide; then gradually heat nearly to boiling, dilute considerably, again pass in hydrogen sulphide until the liquid smells strongly of that gas, allow to stand for about five minutes, and then collect the pp. on a filter.

To make certain that the whole of the metal of Group II. has been precipitated, dilute a part of the filtrate from the pp., heat gently for a few minutes, again pass in hydrogen sulphide, and let stand for a few minutes:—if no pp. is formed, the metal of Group II. has been removed completely.

Collect the pp. produced by hydrogen sulphide on a filter.

Wash the pp. two or three times with warm water.

Observe the colour of the pp. produced by hydrogen sulphide, and then proceed to examine it according to **A, B, or C** (*below*).

A. The pp. is *orange-red*. Remove some of the washed pp. to a test-tube, fill the tube to about one-sixth with *ammonium sulphide*, and warm (don't boil) for a few minutes; if the pp. dissolves, and is re-precipitated (along with finely divided yellowish white sulphur) by adding *excess of hydrochloric acid*, the pp. is Sb_2S_3 , and, therefore, **ANTIMONY** is present.

B. The pp. is *yellow*. To a little of the washed pp. add *ammonium sulphide* and warm (as directed under **A**):—

(1) The yellow pp. does not dissolve in warm *ammonium sulphide*; the pp. is CdS , and, therefore, **CADMIUM** is present.

(2) The yellow pp. dissolves in warm *ammonium sulphide*; the pp. is As_2S_3 or SnS_2 . To another part of the washed yellow pp. add a little water, and a few grams of solid *ammonium carbonate* (to insure that a concentrated solution of this salt is produced), and warm (don't boil) for some minutes.

If the pp. dissolves, and is re-precipitated by adding *excess of hydrochloric acid*, the pp. is As_2S_3 , and, therefore, **ARSENIC** is present.

If the pp. does not dissolve, it is SnS_2 , and, therefore, **TIN** is present as a *stannic* compound.

Confirm this result by boiling another part of the yellow pp. that was produced by

hydrogen sulphide with a little *conc. hydrochloric acid* in a basin, for a few minutes, then adding some water and *copper turnings*, and boiling for at least five minutes; then pouring off the liquid and adding to it a solution of *mercuric chloride*; if a greyish-black pp. forms this pp. is Hg and HgCl , and, therefore, the presence of **TIN** is confirmed. (Reactions: (i.) $\text{SnS}_2 + (4+x)\text{HClAq} = \text{SnCl}_4$ in $x\text{HClAq} + 2\text{H}_2\text{S}$; (ii.) SnCl_4 in $x\text{HClAq} + \text{Cu} = \text{SnCl}_2$ in $x\text{HClAq} + \text{CuCl}_2\text{Aq}$; (iii.) SnCl_2 in $x\text{HClAq} + \text{HgCl}_2\text{Aq} = \text{SnCl}_4$ in $x\text{HClAq} + \text{Hg}$.)

C. The pp. is *black or dark brown*. To a little of the washed pp. add *ammonium sulphide*, and warm (as directed under **A**):—

(1) The dark coloured pp. dissolves in warm *ammonium sulphide*; the pp. is SnS , and, therefore, **TIN** is present as a *stannous* compound.

Confirm this result by adding *dilute hydrochloric acid* to the solution of the pp. in ammonium sulphide, until the liquid is acid; a yellow pp. is SnS_2 (mixed with finely divided yellowish white sulphur).

(2) *The dark coloured pp. does not dissolve in warm ammonium sulphide*; the pp. is HgS , PbS , CuS , or Bi_2S_3 :—

In this case remove *another portion of the washed pp.* to a test-tube, fill the tube to about one-sixth with *nitric acid* (about one part conc. acid to three parts water), and boil for a few minutes.

The dark coloured pp. does not dissolve in the nitric acid :—

Pour about a tenth of a tubeful of *conc. hydrochloric acid* into the test-tube containing the pp. and nitric acid, and boil for some minutes; then add water, and boil again till every trace of hydrogen sulphide is removed; then to this solution add *stannous chloride solution drop by drop*; if a white pp. is produced, and this turns grey, and then black, when more stannous chloride is added, the white pp. is HgCl , and the black pp. is Hg , and, therefore, *Mercury* is present.

NOTE.—Should the pp. produced by hydrogen sulphide consist of PbS , a part of this may be changed to white PbSO_4 by boiling with nitric acid ($\text{PbS} + 8\text{HNO}_3 = \text{PbSO}_4 + 8\text{NO}_2 + 4\text{H}_2\text{O}$); in this case all, or a part, of the white PbSO_4 will be insoluble in *aqua regia*; the reaction for mercury with stannous chloride will not be obtained. Nevertheless if lead is present some of the pp. produced by hydrogen sulphide (PbS) will dissolve in the nitric acid, and lead will be detected in the usual way.

The dark coloured pp. dissolves in nitric acid (small, light, spongy particles of sulphur may float in the liquid, but these may be neglected) :—

Boil the solution in nitric acid till every trace of hydrogen sulphide is removed; then add about one-sixth of a test-tubeful of *dilute sulphuric acid*, and evaporate in a small basin nearly, *but not quite*, to dryness; *let cool*, and then add about quarter a tubeful of water and a very little *dilute sulphuric acid*, pour the liquid into a test-tube and warm for a few minutes; if a white pp. remains this pp. is PbSO_4 , and, therefore, *Lead* is present.¹

If evaporation with dilute sulphuric acid has not produced a pp. (i.e. if lead is absent), to the liquid in the tube add excess of ammonia :—

If a deep blue colour appears in the liquid this is due to formation, in solution, of $\text{CuO} \cdot \text{H}_2\text{O} \cdot 2\text{NH}_3$, and, therefore, *Copper* is present.

If a slight, gelatinous, white pp. is produced this is probably $\text{Bi}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, and, therefore, *bismuth* is probably present.

Confirm this result by collecting the pp. on a filter, washing it, then dissolving it in not more than *twelve drops*, of *boiling dilute hydrochloric acid* (pouring the same acid repeatedly on to the filter), and pouring this solution in to 200 or 300 c.c. of water; if a white cloudy pp. forms in the water, this is BiOCl , and, therefore, *Bismuth* is present.

¹ That this pp. is PbSO_4 may be confirmed by washing the pp., dissolving it

B. If the salt or the metal to be tested is a solid proceed as follows.

(i.) Place a *very little* of the substance in a test-tube, fill the tube to about one-fourth with *water*, and *boil*. If all dissolves, add a *little more* of the substance, *boil till dissolved*, and use this solution as directed under **A** (p. 258).

(ii.) If the substance does not dissolve in water, *boil a very little* with about an eighth of a test-tubeful of *dilute hydrochloric acid*. If all dissolves, add a *little more* of the substance, and a *little more* dilute hydrochloric acid; *boil till all is dissolved*, and use this solution as directed under **A** (p. 258).

(iii.) If the substance does not dissolve in dilute hydrochloric acid, *boil a very little* with about an eighth of a test-tubeful of *conc. hydrochloric acid* for some minutes, then add water, and *boil again*. If all dissolves, treat a *little more* of the substance in the same way with *conc. hydrochloric acid*, and then with water, and use this solution as directed under **A** (p. 258).

Boiling with *conc. hydrochloric acid* converts many metals or salts of metals into chlorides; and these chlorides generally then dissolve on adding water.

(iv.) If the substance does not dissolve by treatment with boiling hydrochloric acid and water, *boil a little* of it with about a quarter of a test-tubeful of *conc. hydrochloric acid* and about one-fourth as much *conc. nitric acid* for some minutes; then pour the whole into a basin, and evaporate nearly, *but not quite*, to dryness; add *about twenty drops* of *conc. hydrochloric acid*, *boil till almost the whole of the acid is removed*, then add some water, and use the solution as directed under **A** (p. 258).

It is absolutely necessary to remove the nitric acid by evaporation, followed by boiling with a little hydrochloric acid, before precipitating the metal in solution by hydrogen sulphide (compare Experiment II. of this Lesson, p. 251).

in hot *ammonium acetate* solution, and adding *potassium chromate* solution, when yellow PbCrO_4 will be precipitated.

LESSON XLV

DETECTION OF A SINGLE METAL KNOWN TO BELONG

TO GROUP III

Materials required.—Solutions of a salt of each of the following metals: aluminium, chromium, iron. A few salts of these metals in solution; also one or two of the metals themselves.

The metals in this group are iron, aluminium, and chromium; iron must be present as a ferric salt. A little $Mn_2O_3 \cdot xH_2O$ may be precipitated in this group; but most of the manganese will remain in solution.

Group reagent is ammonia, added to a solution containing ammonium chloride and free from hydrogen sulphide.

The pps. produced by the group reagent are FeO_3H_3 , AlO_3H_3 , and CrO_3H_3 ; these pps. vary in colour from white to brownish red.

Experiment I.—To become acquainted with the reactions used for detecting a metal of Group III.

To small quantities (about a tenth of a test-tubeful) of solutions of salts of the following metals, aluminium, chromium, and ferric iron, add about an equal volume of ammonium chloride solution, and then excess of ammonia solution. Boil the contents of the three tubes for a minute or two; let the pps. settle, and then pour off the supernatant liquids; to each pp. add a little water, boil, allow to settle, and pour off the liquids.

Collect a portion of each washed pp. on a filter.

To the remainder of the white, jelly-like, pp. of AlO_3H_3 add a good deal of potash solution; the pp. dissolves, $(AlO_3H_3 + KOHAq = KAlO_2Aq + 2H_2O)$; to this solution add about half a test-tubeful of ammonium chloride solution; a gelatinous pp. (of AlO_3H_3) forms and settles very slowly $(KAlO_2Aq + NH_4ClAq + H_2O = AlO_3H_3 + KClAq + NH_3Aq)$.

To the remainder of the greenish white pp. of CrO_3H_3 add a LITTLE potash solution; the pp. does not dissolve. Now add about half a test-tubeful of potash solution; the pp. dissolves. Boil the liquid; CrO_3H_3 is gradually re-precipitated.

To the remainder of the brownish red pp. of FeO_3H_3 add *potash* solution; the pp. does not dissolve. Pour off the liquid from above the pp., and add to the pp. a slight excess of dilute *hydrochloric acid*; the pp. dissolves. To this solution add *potassium ferrocyanide* solution; a deep blue pp. of ferric ferrocyanide (*Prussian blue*) is produced in the liquid.

Make three *borax beads* on platinum wires.¹ On to one bead take a VERY LITTLE of the pp. of AlO_3H_3 which you collected on a filter; on to another bead take a VERY LITTLE of the pp. of CrO_3H_3 ; and on to the third bead take a VERY LITTLE of the pp. of FeO_3H_3 . Heat the beads in the outer part of a non-luminous Bunsen flame until everything is thoroughly melted; then remove the beads from the flame and observe the colour of each, when it is hot, and also when it cools. The bead into which AlO_3H_3 was melted is colourless; the bead into which CrO_3H_3 was melted is emerald-green both when hot and cold; and that into which FeO_3H_3 was melted is reddish yellow when hot, and greenish yellow when cold. (Sodium-aluminium borates, sodium-chromium borates, and sodium-iron borates, are formed in these reactions.)

Synopsis of those Reactions of the Metals of Group III. which are Employed in Detecting one of these Metals.

The pp.
produced
by am-
monia is

(1) *White*, and gelatinous, and soluble in *potash* solution = AlO_3H_3 ; the solution in *potash* (which contains KAlO_2) gives a white pp. of AlO_3H_3 on addition of much *ammonium chloride* solution.

The pp. gives no colour when dissolved in *melted borax*.

(2) *Slaty-green*, and gelatinous, and insoluble in a *little potash* solution = CrO_3H_3 ; the pp. dissolves in *much potash solution*, and is re-precipitated when this solution is boiled for some time.

When the pp. is dissolved in *melted borax* an emerald-green substance is formed.

¹ Made by forming a small loop on the end of a piece of platinum wire, dipping this into borax and heating until the borax melts and becomes quite transparent.

The pp. produced by ammonia is { (3) *Brownish red*, and flocculent, and insoluble in *potash* solution = FeO_3H_3 ; the pp. dissolves in warm *hydrochloric acid*, and this solution gives a deep blue pp. with *potassium ferrocyanide*.

When the pp. is dissolved in *melted borax* a reddish yellow substance is formed, which becomes greenish yellow on cooling.

Before proceeding to make use of the reactions examined in *Experiment I.*, and tabulated in the synopsis of reactions, it is advisable to become acquainted with certain reactions of ferrous and ferric compounds which show that a ferric compound must be present before the group reagent—ammonia added after ammonium chloride—is added to precipitate the metals of Group III.

Experiment II.—To show that the iron compound in a solution to be examined for Group III. must be a ferric compound.

Make a solution in cold water of a little ferrous sulphate, and to this liquid add a good deal (say half a test-tubeful) of ammonium chloride solution, and then excess of ammonia solution. A slight, greenish, pp. is produced; and this pp. turns brown where it is exposed to the air. Throw the pp. on to a filter; the liquid that comes through the filter is muddy, and re-filtration does not clear the liquid. Add a few drops of conc. nitric acid to the muddy filtrate, and boil as long as any change is noticeable in the colour of the liquid; then add excess of ammonia solution to the reddish yellow liquid; the production of a brownish red, flocculent, pp. shows that the liquid filtered from the pp. produced by adding excess of ammonia to the solution of ferrous sulphate contains iron, and that, therefore, the whole of the iron in the solution of ferrous sulphate was not precipitated by ammonia added after ammonium chloride.

Now dissolve a little ferric chloride in water; add ammonium chloride solution, and then excess of ammonia solution; filter off the reddish brown, flocculent, pp. of FeO_3H_3 that forms; to the

filtrate add a slight excess of *hydrochloric acid*, and then a solution of *potassium ferrocyanide*. The fact that no blue pp., or blue colour, is produced shows that the whole of the iron in the ferric compound was precipitated by ammonia added after ammonium chloride.

Experiment III.—*To apply the results of the foregoing experiments to find out what metal is present in a salt which is known to be a salt of aluminium, chromium, or iron; or to find out which of these metals is the metal given you.*

A. If the substance is given in solution proceed as follows. If the substance is a solid see **B** (p. 261).

To about quarter a test-tubeful of the solution add about twenty drops of *conc. nitric acid*, and boil for some minutes (any ferrous compounds present are thus oxidised to ferric compounds); then add a considerable quantity (about quarter a test-tubeful) of *ammonium chloride* solution; and then add an excess of *ammonia* solution (until there is a distinct smell of ammonia when the liquid is thoroughly mixed); boil for a few minutes, and collect the pp. on a filter.

Wash the pp. three or four times with hot water.

Observe the colour and appearance of the pp. and proceed to examine it according to **A**, **B**, or **C** (below).

A. The pp. produced by ammonia is *white*, gelatinous, and semi-transparent. To a portion of the washed pp. in a test-tube add *potash* solution; if the pp. dissolves, and is again formed when a considerable quantity of *ammonium chloride* solution is added to this liquid, the pp. is AlO_3H_3 , and, therefore, ALUMINIUM is present.

Confirm this result by taking a little of the washed pp. on a *borax bead*, and heating in a *non-luminous* Bunsen flame until melted; the bead remains clear and colourless.

B. The pp. produced by ammonia is *greyish green*, and gelatinous. To a portion of the washed pp. add a considerable quantity (about a test-tubeful) of *potash* solution; if the pp. dissolves to a greenish liquid, from which the original pp. is formed *after boiling for some time*, the pp. is CrO_3H_3 , and, therefore, CHROMIUM is present.

Confirm this result by heating a little of the washed pp. on a borax bead in a non-luminous Bunsen flame until the whole melts; the bead is coloured emerald-green.

C. The pp. produced by ammonia is *brownish red*, and flocculent; it is FeO_3H_3 , and, therefore, Iron is present.

Confirm this result by heating a little of the washed pp. on a borax bead in a non-luminous Bunsen flame until the whole melts; the borax bead is coloured reddish yellow when hot, and the colour changes to greenish yellow as the bead cools. Also confirm by dissolving a little of the washed pp. produced by ammonia in warm dilute hydrochloric acid, adding potassium ferrocyanide solution to this liquid, and getting a deep blue pp. of Prussian blue, $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$.

NOTE TO GROUP III.—When iron is found in this group the original substance should be examined to determine whether it contains a ferrous or a ferric compound. For this purpose, to small separate portions of the original solution, or to small separate portions of the original solid dissolved in water or in dilute cold hydrochloric or sulphuric acid, add (1) *potassium sulphocyanide* solution, (2) *potassium ferricyanide* solution (freshly prepared).

Potassium sulphocyanide reacts with ferric salts to form deep red ferric sulphocyanide $[\text{Fe}(\text{CNS})_3]$, which remains in solution; no visible change occurs with ferrous salts.

Potassium ferricyanide reacts with ferrous salts to form a blue pp. of ferrous ferricyanide; with ferric salts this reagent produces a slight brownish colour.

B. If the substance to be tested is a solid, proceed as follows:—

(i.) Place a *very little* of the substance in a test-tube, fill the tube to about one-fourth with *water* and boil. If all dissolves, add a *little more* of the substance, boil till dissolved, and use this solution as directed under **A.** (p. 260).

(ii.) If the substance does not dissolve in water, boil a *very little* with about an eighth of a test-tubeful of *dilute hydrochloric acid*. If all dissolves, add a *little more* of the substance

and a *little more* dilute hydrochloric acid, boil till all is dissolved, and use this solution as directed under **A** (p. 260).

(iii.) If the substance does not dissolve in dilute hydrochloric acid, boil a *very little* with about an eighth of a test-tubeful of *conc. hydrochloric acid* for some minutes, then add water, and boil again. If all dissolves, treat a *little more* of the substance in the same way with *conc. hydrochloric acid* and then with water, and use this solution as directed under **A** (p. 260).

Boiling with *conc. hydrochloric acid* converts many metals or salts of metals into chlorides; and these chlorides generally then dissolve on adding water.

(iv.) If the substance does not dissolve by treatment with boiling hydrochloric acid and water, boil a *little* of it with about a quarter of a test-tubeful of *conc. hydrochloric acid* and about one-fourth as much *conc. nitric acid* for some time; then evaporate in a basin nearly, *but not quite*, to dryness; add *about twenty drops of conc. hydrochloric acid*, boil till most of the acid is removed, then add some water, and use the solution as directed under **A** (p. 260).

LESSON XLVI

DETECTION OF A SINGLE METAL KNOWN TO BELONG TO
GROUP IV

Materials required.—Solutions of a salt of each of the following metals: cobalt, manganese, nickel, zinc. A few salts of these metals in solution; also a few solid salts of the metals.

The metals in this group are *cobalt, nickel, manganese, and zinc.*

Group reagent is ammonium sulphide, added to an alkaline solution containing ammonium chloride.

The pps. produced by the group reagent are CoS , NiS , MnS , and ZnS ; these pps. vary in colour from white to black.

Experiment I.—*To become acquainted with the reactions used for detecting a metal of Group IV.*

To small quantities (about a tenth of a test-tubeful) of solutions of salts of cobalt, nickel, manganese, and zinc, add about an equal volume of *ammonium chloride* solution, then excess of *ammonia* solution, and then *six or eight drops* (not more) of a solution of *ammonium sulphide*. Boil the contents of each tube for some minutes; let the pps. settle; pour off the supernatant liquids; to each pp. add a little water, boil, allow to settle, and pour off the liquids.

Collect a *portion* of each washed pp. on a filter.

To the remainder of each pp. add about a tenth of a test-tubeful of dilute hydrochloric acid, and mix the contents of the tubes by shaking thoroughly. The buff-coloured pp. of MnS , and the white pp. of ZnS , dissolve gradually (the liquids probably remain turbid from the presence of a little sulphur in them: $\text{MnS} + 2\text{HClAq} = \text{MnCl}_2\text{Aq} + \text{H}_2\text{SAq}$; a little H_2S is oxidised with separation of sulphur). The black pps. of CoS and NiS are not changed.

Now boil the solutions of the sulphides of manganese and

zinc in hydrochloric acid until hydrogen sulphide ceases to be given off; then cool the liquids thoroughly, and to each add *potash* solution, *drop by drop*; a brownish white pp. (MnO_2H_2 rapidly changing in the air to $\text{Mn}_2\text{O}_3 \cdot x\text{H}_2\text{O}$) forms in the solution of manganese chloride, and a white gelatinous pp. (ZnO_2H_2) in the solution of zinc chloride. Add more *potash* solution to these pps.; the pp. of ZnO_2H_2 gradually dissolves ($\text{ZnO}_2\text{H}_2 + (2+x)\text{KOH} \text{Aq} = \text{ZnO}_2\text{K}_2\text{Aq} + 2\text{H}_2\text{O} + x\text{KOH} \text{Aq}$), but the pp. of hydrated manganese oxides does not dissolve.

Turn back to the four pps. you collected on filters. Examine each pp. by the *borax bead test* (for details see p. 258): the bead heated with CoS is coloured deep blue; that heated with NiS is coloured pinkish brown; that heated with MnS is coloured amethyst; and that heated with ZnS remains uncoloured. Now take a *little* of the pp. of ZnS on to a loop formed on the end of a piece of *clean* platinum wire; heat this for a minute or so; then let a drop of *cobalt nitrate* solution fall on to it, and heat again to full redness for some time: the solid on the platinum wire is coloured green (compounds of oxides of zinc and cobalt are produced).

Synopsis of those Reactions of the Metals of Group IV. which are Employed in Detecting one of these Metals.

The pp. produced by ammonium sulphide is

- (1) *Black*, and does not dissolve in *cold dilute hydrochloric acid* = CoS or NiS .
 - (a) CoS gives a blue colour when dissolved in *melted borax*.
 - (b) NiS gives a pinkish brown colour when dissolved in *melted borax*.
- (2) *Buff-coloured*, and dissolves in *cold dilute hydrochloric acid* = MnS ; the solution in hydrochloric acid, after being boiled till hydrogen sulphide is removed, gives a brownish white pp. with *potash* solution, and this pp. does not dissolve when more *potash* solution is added. The pp. gives an amethyst colour when dissolved in *melted borax*.

The pp. produced by ammonium sulphide is

(8) *White* (appearing yellowish in the yellow liquid), and dissolves in *cold dilute hydrochloric acid* = ZnS ; the solution in hydrochloric acid, after being boiled till hydrogen sulphide is removed, gives a white pp. with a *little potash* solution, and this pp. dissolves in *much potash* solution. The pp. gives no colour when dissolved in *melted borax*; but it is coloured green when it is heated, then moistened with *cobalt nitrate* solution, and again heated strongly.

Experiment II.—*To apply the results of the foregoing experiments to find out what metal is present in a salt which is known to be a salt of cobalt, manganese, nickel, or zinc; or to find out which of these metals is the metal given you.*

A. If the substance is given in solution proceed as follows. If the substance is a solid see **B** (p. 266).

To about quarter a test-tubeful of the solution add a little *ammonium chloride* solution, then excess of *ammonia* solution, and then add *about ten drops* of *ammonium sulphide*, boil for five minutes or so (boiling makes the pp. granular, and also removes excess of ammonium sulphide wherein NiS is slightly soluble), and then collect the pp. on a filter.

Wash the pp. three or four times with warm water.

Observe the colour and appearance of the pp. and proceed to examine it according to **A**, **B**, or **C** (below).

A. The pp. is *black*. Transfer a *portion* of the washed pp. to a test-tube, fill the test-tube to about one-sixth with *dilute hydrochloric acid*, and shake for a few minutes, without warming; if the pp. does not dissolve it is CoS or NiS . Heat a *little* of the washed pp. on a *borax bead* in a non-luminous Bunsen flame until the whole melts.

If the bead is coloured deep blue the pp. was CoS , and, therefore, **COBALT** is present.

If the bead is coloured pinkish brown the pp. was NiS , and, therefore, NICKEL is present.

B. The pp. produced by ammonium sulphide is *buff-coloured*. Shake a *portion* of the washed pp. with *dilute hydrochloric acid*, without warming; if the pp. dissolves (a little whitish sulphur will probably be formed), boil the solution until every trace of hydrogen sulphide is removed, then *cool the liquid*, and add *potash* solution to it; if a brownish white pp. is formed which does not dissolve in more potash solution, this pp. is $\text{Mn}_2\text{O}_3 \cdot x\text{H}_2\text{O}$, and, therefore, MANGANESE is present.

Confirm this result by heating a *little* of the washed pp. produced by ammonium sulphide on a *borax bead* in a non-luminous Bunsen flame till the whole melts; the bead is coloured reddish violet.

C. The pp. produced by ammonium sulphide is *white*; it will appear yellowish as the liquid is coloured yellow by ammonium sulphide. Shake a *portion* of the washed pp. with *dilute hydrochloric acid*, without warming; if the pp. dissolves (a little whitish sulphur will probably be formed), boil the solution until every trace of hydrogen sulphide is expelled, then *cool the liquid*, and to the cold liquid add *potash* solution, *drop by drop*; if a white, gelatinous, semi-transparent, pp. is produced, and this pp. dissolves when a good deal of potash solution is added, this pp. is ZnO_2H_2 , and, therefore, ZINC is present.

Confirm this result by heating a *little* of the washed pp. produced by ammonium sulphide on a *borax bead* in a non-luminous Bunsen flame until the whole melts; the bead remains colourless. *Also confirm* by heating a little of the pp. produced by ammonium sulphide on platinum wire, then moistening with a drop of *cobalt nitrate* solution, and again heating strongly for some minutes; the solid on the wire is coloured green.

B. If the substance to be tested is a solid proceed as follows:—

(i.) Place a *very little* of the substance in a test-tube, fill the tube to about one-fourth with *water*, and, boil. If all dissolves, add a *little more* of the substance, boil till dissolved, and use this solution as directed under **A** (p. 265).

(ii.) If the substance does not dissolve in water, boil a *very little* with about an eighth of a test-tubeful of *dilute hydrochloric acid*. If all dissolves, add a *little more* of the substance and a *little more* dilute hydrochloric acid, boil till all is dissolved, and use this solution as directed under **A** (p. 265).

(iii.) If the substance does not dissolve in dilute hydrochloric acid, boil a *very little* with about one-eighth of a test-tubeful of *conc. hydrochloric acid* for some minutes, then add water, and boil again. If all dissolves, treat a *little more* of the substance in the same way with conc. hydrochloric acid, and then with water, and use this solution as directed under **A** (p. 265).

Boiling with conc. hydrochloric acid converts many metals or salts of metals into chlorides; and these chlorides generally then dissolve on adding water.

(iv.) If the substance does not dissolve by treatment with boiling hydrochloric acid and water, boil a *little* of it with about a quarter of a test-tubeful of *conc. hydrochloric acid* and about one-fourth as much *conc. nitric acid* for some minutes; pour the whole into a basin, and evaporate, nearly, *but not quite*, to dryness; add *about twenty drops* of *conc. hydrochloric acid*, boil till most of the acid is removed, then add some water, and use this solution as directed under **A** (p. 265).

LESSON XLVII

DETECTION OF A SINGLE METAL KNOWN TO BELONG TO
GROUP V

Materials required.—Solutions of a salt of each of the following metals : barium, calcium, and strontium. A few salts of these metals, some solid and some in solution.

The metals in this group are *barium, strontium, and calcium.*

Group reagent is ammonium carbonate, added to an alkaline solution containing ammonium chloride.

The pps. produced by the group reagent are BaCO_3 , SrCO_3 , and CaCO_3 ; these pps. are white.

Experiment I.—*To become acquainted with the reactions used for detecting a metal of Group V.*

To small quantities (about a tenth of a test-tubeful) of solutions of salts of barium, calcium, and strontium, add a little ammonium chloride solution, then a slight excess of ammonia solution, and then ammonium carbonate solution. Boil the contents of each tube; let the pps. settle; pour off the supernatant liquids; to each pp. add a little water, boil, allow to settle, and pour off the liquids.

Collect a *portion* of each washed pp. on a filter.

To the *remainder* of each pp. add *acetic acid* solution; the pps. dissolve with effervescence (CO_2 is given off). To a *little* of each solution in acetic acid add a solution of *potassium chromate*; a yellow pp. forms in the tube containing barium acetate; the other liquids remain clear. Dilute the remainder of the solutions of the three carbonates in acetic acid with about their own bulk of water, and then add to each about *eight or ten drops* of *VERY dilute sulphuric acid*; white barium sulphate is at once precipitated from the solution of barium acetate; the solutions containing calcium and strontium acetates remain clear.

Now *boil* these two solutions; white strontium sulphate is gradually precipitated, but no pp. forms in the tube containing the calcium salt mixed with a little sulphuric acid. (These reactions are based on the different solubilities in very dilute sulphuric acid of the sulphates of barium, strontium, and calcium.)

Now clean a piece of platinum wire;¹ see that no tinge of colour is imparted to a non-luminous flame by the wire. Take a small quantity of the washed pp. of barium carbonate from the filter on which it has been collected (see above) on to the wire and bring it into the non-luminous flame; the flame is coloured grass-green. Examine the other pps. in the same way (cleaning the wire *thoroughly* each time); the strontium salt imparts a crimson colour (appearing rose-purple through blue glass), and the calcium salt a yellowish red colour (appearing green-grey through blue glass), to the flame.

Synopsis of those Reactions of the Metals of Group V. which are Employed in Detecting one of these Metals.

The pp. produced by ammonium carbonate is *white*, and dissolves in acetic acid. A solution in acetic acid of a salt of barium gives a yellow pp. (BaCrO_4) with *potassium chromate* solution; a solution in acetic acid of a salt of strontium or of calcium gives no pp. with *potassium chromate*.

When a *dilute solution* of a salt of strontium is boiled with a *very little dilute sulphuric acid*, white strontium sulphate is gradually precipitated; when *dilute sulphuric acid* is added to a solution of a salt of barium, a white pp. of barium sulphate is produced *at once, and without boiling*; when a *dilute solution* of a salt of calcium is boiled with a *very little dilute sulphuric acid*, no pp. is produced.

A solid compound of barium gives a grass-green colour to a non-luminous flame in which it is volatilised; a solid compound of strontium gives a crimson colour, appearing rose-purple when

¹ The wire should be scraped with a clean knife, then dipped into conc. hydrochloric acid in a test-tube, and then heated in the flame. Dipping into the acid, and heating, must be repeated until not a trace of colour is imparted to the flame.

looked at through a piece of blue glass, and a solid compound of calcium gives a yellowish red colour, appearing greenish grey through a blue glass, to a non-luminous flame.

Experiment II.—*To apply the foregoing reactions to find out what metal is present in a salt which is known to be a salt of barium, calcium, or strontium.*

A. If the substance is given in solution proceed as follows. *If the substance is a solid see B (p. 271).*

To about quarter a test-tubeful of the solution add a little ammonium chloride solution, then a slight excess of ammonia solution, and then ammonium carbonate solution, boil for a minute or so, and then collect the pp. on a filter.

Wash the pp. three or four times with hot water.

Transfer about three-fourths of the washed pp. to a test-tube and dissolve it in as little acetic acid as possible.

(1) To one portion of the solution of the pp. in acetic acid add potassium chromate solution, and warm; a yellow pp. is BaCrO_4 , and, therefore, BARIUM is present.

Confirm this result by placing a little of the washed pp. produced by ammonium carbonate on a piece of clean platinum wire, moistening with conc. hydrochloric acid, and bringing the moistened substance into a non-luminous Bunsen flame; after a short time the flame will be coloured grass-green.

Also confirm the presence of barium by adding dilute sulphuric acid to another portion of the solution in acetic acid of the pp. produced by ammonium carbonate, and getting a white pp. of BaSO_4 which forms immediately.

(2) *If barium is absent, to another portion of the solution in acetic acid of the pp. produced by ammonium carbonate add about an equal bulk of water and then ten or twelve drops (not more) of dilute sulphuric acid, and boil for a few minutes; a white pp., forming gradually, is SrSO_4 , and, therefore, STRONTIUM is present. If no pp. forms on boiling see (8).*

Confirm this result by trying the flame test with a little of the washed pp. after moistening with conc. hydrochloric

acid (see under (1)); the flame is coloured crimson, and viewed through a blue glass the colour is purplish rose.

(8) If neither barium nor strontium is present, examine the washed pp. produced by ammonium carbonate by the *flame test* (see under (1), p. 270); if the flame is coloured red, appearing greenish grey when looked at through a blue glass, CALCIUM is present.

B. If the substance to be tested is a solid proceed as follows:—

(i.) Place a *very little* of the substance in a test tube, fill the tube to about one-fourth with *water* and boil. If all dissolves, add a *little more* of the substance, boil till dissolved, and use this solution as directed under **A** (p. 270).

(ii.) If the substance does not dissolve in water, boil a *very little* with about an eighth of a test-tubeful of *dilute hydrochloric acid*. If all dissolves, add a *little more* of the substance and a *little more* dilute hydrochloric acid, boil till all is dissolved, and use this solution as directed under **A** (p. 270).

(iii.) If the substance does not dissolve in dilute hydrochloric acid, boil a *very little* with about an eighth of a test-tubeful of *conc. hydrochloric acid* for some minutes, then add water, and boil again. If all dissolves, treat a *little more* of the substance in the same way with *conc. hydrochloric acid* and then with water, and use the solution as directed under **A** (p. 270).

Boiling with *conc. hydrochloric acid* converts many metals or salts of metals into chlorides; and these chlorides generally then dissolve on adding water.

(iv.) If the substance does not dissolve by treatment with boiling hydrochloric acid and water, boil a *little* of it with about a quarter of a test-tubeful of *conc. hydrochloric acid* and about one-fourth as much *conc. nitric acid* for some minutes; pour the whole into a basin, and evaporate, nearly, *but not quite*, to dryness; add *about twenty drops of conc. hydrochloric acid*, boil till most of the acid is removed, then add some water, and use the solution as directed under **A** (p. 270).

LESSON XLVIII.

DETECTION OF A SINGLE METAL KNOWN TO BELONG TO
GROUP VI

Materials required.—Solutions of a salt of each of the following metals: ammonium, magnesium, potassium, and sodium. A few salts of these metals, some solid and some in solution.

There is *no group reagent* for the metals in this group; the metals are *magnesium,¹ potassium, sodium, and ammonium.*

Experiment I.—*To become acquainted with the reactions used for detecting a metal of Group VI.*

To a *small quantity* of a compound of ammonium add a little *potash* solution and boil; ammonia is given off, recognised by its smell, and its turning to blue the colour of red litmus paper held in the steam issuing from the tube. Boil a *small quantity* of an ammonium compound with a *little conc. hydrochloric acid* for a minute or two, and then add some *platinic chloride* solution; a yellow-red crystalline pp. $(\text{NH}_4)_2\text{PtCl}_6$ is formed, and this pp. is insoluble in *alcohol*. Heat a very little of an ammonium compound on a crucible lid to *full redness*; the compound is volatilised and disappears.

Boil a *small quantity* of a compound of potassium with a *little conc. hydrochloric acid* for a minute or two (the compound is thus changed to chloride of potassium), and then add some *platinic chloride* solution; a yellow-red crystalline pp. $(\text{K}_2\text{PtCl}_6)$ is formed, and this pp. is insoluble in *alcohol*. To a *conc. aqueous* solution of a compound of potassium add *sodium-hydrogen tartrate* solution, and shake; a white, crystalline pp. $(\text{KHC}_4\text{H}_4\text{O}_6)$ is formed. Heat a little of a potassium compound to *full redness*

¹ In the experiments on the grouping of the metals (*Lesson XLI.*) magnesium is placed in a group by itself.

on a crucible lid; the compound does not disappear. Take a *very little* of a compound of potassium on to a piece of *clean platinum wire* (see note, p. 269), and bring it into a *non-luminous* Bunsen flame; the flame is coloured lavender-violet; look at this flame through a *thick piece of blue glass*—you see that the colour appears purple-violet. Bring a *very little* of a compound of sodium into a *non-luminous flame*; the flame is coloured intense yellow; look at this flame through a *thick piece of blue glass*, and you notice that scarcely any colour is to be seen.¹ To a little of an aqueous solution of a sodium compound add *potassium pyroantimonate* solution; a white, crystalline pp. ($\text{Na}_2\text{H}_2\text{Sb}_2\text{O}_7$) forms gradually.

To two small quantities of an aqueous solution of a magnesium compound add (i.) *ammonia* solution; (ii.) *ammonium carbonate* solution; in each case a white pp. is produced (the pp. by ammonia is $\text{MgO} \cdot x\text{H}_2\text{O}$, the pp. produced by ammonium carbonate is $\text{MgCO}_3 \cdot x\text{H}_2\text{O}$, or it may be $\text{MgCO}_3 \cdot (\text{NH}_4)_2\text{CO}_3 \cdot x\text{H}_2\text{O}$). Let the pps. settle, pour off the supernatant liquids, and add to each pp. a solution of *ammonium chloride*; both pps. dissolve ($\text{MgCl}_2 \cdot 2\text{NH}_4\text{Cl}$ is formed and goes into solution). To a third small quantity of an aqueous solution of a magnesium compound add about its own bulk of a solution of *ammonium chloride*, and then a slight excess of *ammonia*; no pp. is formed: now add *sodium phosphate* solution, and shake; a white, crystalline pp. (MgNH_4PO_4) forms gradually.

Synopsis of those Reactions of the Metals of Group VI. which are Employed in Detecting one of these Metals.

Ammonia is given off when a compound of ammonium is boiled with *potash* solution. Ammonium compounds after being boiled with hydrochloric acid give a yellowish red crystalline pp. ($(\text{NH}_4)_2\text{PtCl}_6$) with *platinum tetrachloride*, insoluble in *alcohol*. Ammonium compounds are *readily volatilised*.

Sodium compounds colour a non-luminous flame *deep yellow*, and the colour almost disappears when the flame is looked at through a blue glass.

¹ The non-luminous flame of a Bunsen lamp should be observed through the blue glass; the flame appears slightly violet, but the colour is not so red-violet as that of a flame in which a compound of potassium is volatilised.

Sodium compounds in aqueous solution give a white crystalline pp. ($\text{Na}_2\text{H}_2\text{Sb}_2\text{O}_7$) with *potassium pyroantimonate* solution.

Potassium compounds colour a non-luminous flame *lavender-violet*, and the colour appears *purple-violet* when the flame is looked at through a *thick piece of blue glass*.

Potassium compounds after being boiled with conc. hydrochloric acid give a yellow-red crystalline pp. (K_2PtCl_6) with *platinum tetrachloride*; the pp. is insoluble in *alcohol*.

Potassium compounds in conc. aqueous solution give a white crystalline pp. ($\text{KH.C}_4\text{H}_4\text{O}_6$) with solution of *sodium-hydrogen tartrate*.

Magnesium compounds in solution give a white granular pp. (of MgNH_4PO_4) with *sodium phosphate*; this pp. forms slowly; it is insoluble in *ammonium chloride* solution.

Experiment II.—To apply the foregoing reactions to find out what metal is present in a salt which is known to be a salt of magnesium, potassium, sodium, or ammonium.

Dissolve some of the salt in water, or in dilute hydrochloric acid.

(1) To a portion of the solution add about quarter a test-tubeful of *ammonium chloride* solution, then a slight excess of *ammonia* solution, and then some *sodium phosphate* solution, and shake vigorously for a little time. If a white granular pp. forms gradually this pp. is MgNH_4PO_4 , and, therefore, **MAGNESIUM** is present.

(2) To another portion of the solution add *potassium pyroantimonate* solution, and shake; if a white crystalline pp. is produced this pp. is *sodium pyroantimonate* ($\text{Na}_2\text{H}_2\text{Sb}_2\text{O}_7$), and, therefore, **SODIUM** is present.

Confirm this result by bringing a little of the original solid, or of the solution boiled down nearly to dryness, supported on a piece of *clean platinum wire*, into a non-luminous flame; the flame is coloured deep yellow, and the colour disappears, except a faint violet (see note, p. 278), when the flame is looked at through a *thick piece of blue glass*.

(3) Concentrate another portion of the solution till its bulk

does not exceed a few c.c., and then add to it a solution of *sodium-hydrogen tartrate*, and shake; if a white crystalline pp. forms this pp. is potassium-hydrogen tartrate ($\text{KH. C}_4\text{H}_4\text{O}_6$), and, therefore, POTASSIUM is present.

Confirm this result by bringing a little of the original solid, or of the solution boiled down nearly to dryness, supported on a piece of *clean* platinum wire, into a non-luminous flame; the flame is coloured lavender-violet, and the colour looks purple-violet when the flame is looked at through a *thick piece of blue glass*.

Also confirm the result by boiling a little of the solution with *conc. hydrochloric acid*, then adding *platinic chloride* solution and *alcohol*; a yellow-red crystalline pp. (K_2PtCl_6) is produced.

NOTE.—When this confirmatory test with *platinic chloride* for potassium has to be applied to a solution that is being examined for *all the groups*, some of the filtrate from Group V. must be evaporated to dryness, and the residue must be *heated strongly* (best in a platinum capsule) *until volatilisation ceases*; the solid that is left must be boiled with *conc. hydrochloric acid*, and *platinic chloride* solution and *alcohol* must be added to this liquid. [Ammonium compounds give a yellow-red pp. with PtCl_4Aq ; these compounds are volatilised by heat.]

(4) Boil some of the solution, or of the original solid, with a little *potash* solution; if ammonia is given off, recognised by its smell and by its turning blue a piece of red litmus paper held in the steam coming from the tube, AMMONIUM is present.

LESSON XLIX

DETECTION OF METALS WHEN NOT MORE THAN A SINGLE
METAL IS PRESENT IN ANY ONE GROUP

THE principles of the method have been illustrated very fully in the preceding lessons of this section.

It is necessary first to find the groups to which the metals belong; and then to examine each group pp. in order to discover the individual metal contained therein.

As the original substance is a mixture the confirmatory tests for this or that metal cannot be applied to that substance, except in a very few cases. The confirmatory tests must be applied to the group pps., or to solutions of these pps., after the pps. have been collected on filters and washed free from the liquids which adhere to them, which liquids contain salts of metals other than that one metal it is desired to detect in each group pp.

The following directions are applicable to mixtures of the commoner metals, and to mixtures of salts of such metals, provided that the mixtures do not contain more than a single metal in any one group. Mixtures the constituents of which are such that the reactions of some are greatly modified by the presence of others are not considered here.

Substances which are insoluble in water, hydrochloric acid, and *aqua regia*, are not dealt with in these directions; for the qualitative analysis of INSOLUBLE SUBSTANCES see *the end of this Lesson* (p. 285).

A. THE SUBSTANCE TO BE ANALYSED IS A
SOLUTION

Add the group reagents, and examine the pps. produced, by following carefully the directions given in the preceding

lessons. Consult the references and the notes on p. 282 under the heading EXAMINATION OF THE SOLUTION, FOR METALS.

B. THE SUBSTANCE TO BE ANALYSED IS A SOLID

The first thing to be done is to dissolve the substance.

The preparation of a solution must be conducted in a methodical manner.

Most chlorides, almost all normal nitrates, and many other salts, are soluble in water. Many salts, and metals, are converted into chlorides by boiling with diluted, or with concentrated, hydrochloric acid; and most of the chlorides so produced dissolve when water is added. *Aqua regia* (a mixture of conc. hydrochloric and nitric acids) converts most metals, and salts, into chlorides, and the salts generally dissolve when water is added.

I. Boil a VERY LITTLE of the substance, in fine powder, with a little water in a test-tube.

If all dissolves add a little more of the substance, and boil till dissolved, adding more water if necessary.

Examine the solution as directed under the heading EXAMINATION OF THE SOLUTION, FOR METALS (p. 282).

If all does not dissolve proceed to II.

II. *If the substance does not altogether dissolve in water*, boil a VERY LITTLE of it with a little diluted hydrochloric acid for some minutes, or as long as a visible reaction proceeds.

If all does not dissolve proceed to III. (p. 278).

If all dissolves add a little more of the substance, and boil till dissolved, adding a little more diluted hydrochloric acid if necessary; then add about half a test-tubeful of water and allow to cool.

Three cases now present themselves:—

A. A white crystalline pp. forms which soon settles to the bottom of the tube. This pp. is almost certainly PbCl_2 .¹

In this case collect the pp. on a filter.

¹ Lead chloride is slightly soluble in hot dilute hydrochloric acid, but it is considerably less soluble in the same acid when cold; if a small quantity of a lead salt is present in the original substance, the lead chloride that is formed by boiling the original with dilute hydrochloric acid will go into solution; but the greater part of this lead chloride will precipitate as the solution cools.

Set aside the filtrate for examination for Groups II. and onwards. See references and notes on p. 282 under the heading EXAMINATION OF THE SOLUTION, FOR METALS. Wash the pp. on the filter twice with *very small quantities* of COLD water, then remove it to a test-tube, add water, and boil. If the pp. dissolves in boiling water, and this solution gives a yellow pp. with *potassium chromate* solution, LEAD is present. [Compare synopsis of reactions of metals of *Group I.* (p. 245), and directions for applying these reactions (p. 246).]

B. A white amorphous pp. forms which does not settle quickly. This pp. is almost certainly an oxychloride of antimony or of bismuth¹; in this case the pp. will dissolve if the liquid is heated, and antimony or bismuth will be found in its proper place in *Group II.*

Proceed to the examination of this liquid for Groups II. and onwards. See references and notes on p. 282 under the heading EXAMINATION OF THE SOLUTION, FOR METALS.

C. No pp. forms. In this case there is almost certainly no metal of *Group I.* in the original substance, except possibly a *very little lead*; (lead chloride is not quite insoluble in dilute cold hydrochloric acid). If any lead is present it will be found in *Group II.* Neither antimony nor bismuth is likely to be present.

Proceed to the examination of this liquid for Groups II. and onwards. See references and notes on p. 282 under the heading EXAMINATION OF THE SOLUTION, FOR METALS.

III. If the substance does not altogether dissolve in diluted hydrochloric acid, boil about the quantity indicated in fig. 37 (see footnote)² with about a fourth of a test-tubeful of

¹ The solution of a salt of antimony, or a salt of bismuth, in hydrochloric acid will contain antimony chloride, or bismuth chloride; these salts react with water to form oxychlorides which are insoluble in *very dilute* hydrochloric acid. [BiCl_3 in $x \text{HClAq} + (1+y) \text{H}_2\text{O} = \text{BiOCl} + (x+2) \text{HClAq} + y \text{H}_2\text{O}$; SbCl_3 in $x \text{HClAq} + (1+y) \text{H}_2\text{O} = \text{SbOCl} + (x+2) \text{HClAq} + y \text{H}_2\text{O}$.]

² The quantity indicated in fig. 37 is about the proper quantity of substance to use for dissolving in acid. The figure represents the closed end of a test-tube, on the actual scale, with a powdered solid in it.

concentrated hydrochloric acid for some minutes, or as long as a visible reaction proceeds [if the original is a metal, or a mixture of metals, a considerable time may be required, and it may be necessary to add a second dose of acid]; then add about an equal bulk of water, and boil again for a few minutes.

Many metals, and salts of metals, are changed to chlorides by boiling with conc. hydrochloric acid; some chlorides are insoluble in conc. hydrochloric acid, but most dissolve when water is added.



FIG. 37

If all does not dissolve proceed to IV.

If all dissolves allow to cool, and then add a little more water; three cases present themselves:—

- A. A white crystalline pp., which soon settles, forms in the cooling liquid. This pp. is almost certainly PbCl_2 . Proceed as directed under II. A, p. 277.
- B. A white amorphous pp., which settles very slowly, forms. This pp. is almost certainly SbOCl or BiOCl . Proceed as directed under II. B, p. 278.
- C. No pp. forms, even when the liquid is cold. See II. C, p. 278, and proceed as directed there.

IV. If the substance does not altogether dissolve in conc. boiling hydrochloric acid followed by boiling with water, place about the quantity indicated in fig. 37 (see footnote², p. 278) in a small basin, add about a fourth of a test-tubeful of conc. hydrochloric acid and about one-third as much conc. nitric acid, and boil until most but not quite all of the acid is removed. (See note, p. 281).

If the original is a metal, or a mixture of metals, a second, and possibly a third, dose of acid may have to be added to complete the decomposition of the original substance.

Now add to the contents of the basin about half a test-tubeful of water, boil again for a few minutes, and pour the hot liquid through a filter; wash the solid on the filter (if there is any) once with boiling water, and add the washings to the filtrate.

All the commoner metals, except antimony and tin, and most salts, are changed to chlorides by boiling with *aqua regia*; and the chlorides that are produced (except silver chloride) dissolve when

water is added and the liquid is boiled. When antimony is boiled with *aqua regia* white antimonious oxide, Sb_2O_3 (sometimes mixed with a little Sb_2O_5), is formed; and when tin is boiled with *aqua regia* white stannous oxide, SnO_2 , is produced; these oxides are insoluble in solutions of acids.

There may now be two things to be examined: the white solid left on the filter, and the filtrate which has run through the filter. We shall examine the white solid, and then the filtrate. For examination of the filtrate see p. 281.

EXAMINATION OF THE WHITE SOLID produced by boiling the original substance with *aqua regia*.

*It is only when the original is a metal or a mixture of metals that there may be a white solid to be examined here; the solid must be either antimonious or stannous oxide.*¹

Remove some of the solid to a test-tube, add water, boil, let the solid settle, and pour off as much of the supernatant liquid as you can; repeat this washing process with boiling water until the liquid poured off does not redden litmus paper.

As this washing process takes some time, because the solid settles slowly, it is advisable to proceed with the examination of the liquid filtered from the solid (see p. 281) while the washing of the solid is being conducted.

Now pour on to the washed solid about quarter a test-tubeful of a conc. solution of potassium-hydrogen tartrate, boil for three or four minutes, filter (if necessary), and pass hydrogen sulphide into the filtrate until the liquid smells of the gas. If an orange-red pp. forms, this pp. is Sb_2S_3 , and, therefore, ANTIMONY is present.

Antimonious oxide dissolves gradually in a hot solution of potassium-hydrogen tartrate; the solution contains tartar emetic, and gives a pp. of Sb_2S_3 with hydrogen sulphide. Stannous oxide is not changed by heating it with a solution of potassium-hydrogen tartrate. If the solid obtained by heating the original metal, or mixture of metals, with *aqua regia* is not washed thoroughly, the liquid obtained by heating this solid with potassium-hydrogen tartrate solution may contain some other metals besides antimony, and the presence of these other metals may modify the pp. produced by hydrogen sulphide.

If antimony is not found the white solid is stannous oxide.

¹ The possibility of this white solid being silver chloride is not considered here.

To confirm this conclusion transfer the washed solid to a basin, add about half a test-tubeful of *conc. hydrochloric acid* and some *copper* turnings, and boil for at least five minutes; then add a little *water*, allow the solid to settle, pour the liquid through a filter, and to the filtrate add a solution of *mercuric chloride*. If a white pp. forms this pp. is HgCl ; if a greyish black pp. forms this pp. is HgCl mixed with Hg ; in either case TIN is present.

The reactions which occur in this confirmatory test may be represented by the following equations:—(i.) $\text{SnO}_2 + (4 + x) \text{HClAq} + \text{Cu} = \text{SnCl}_2$ in $x \text{HClAq} + \text{CuCl}_2$ in $x \text{HClAq} + 2\text{H}_2\text{O}$;
 { (ii.) SnCl_2 in $x \text{HClAq} + 2\text{HgCl}_2 \text{Aq} = \text{SnCl}_4$ in $x \text{HClAq} + 2\text{HgCl}$ }
 { (iii.) $2\text{HgCl} + \text{SnCl}_2$ in $x \text{HClAq} = \text{SnCl}_4$ in $x \text{HClAq} + 2\text{Hg}$. }

EXAMINATION OF THE FILTRATE from the solid produced by boiling the original substance with *aqua regia*.

This liquid contains nitric acid, which must be removed before the reaction of the liquid with hydrogen sulphide is examined; because nitric acid and hydrogen sulphide decompose one another (see *Lesson XLIV, Experiment II.*, p. 251).

Place the liquid in a basin, and evaporate over a low flame until not more than about one-eighth of a test-tubeful of liquid remains; then add about as much *conc. hydrochloric acid* as the bulk of liquid in the basin, and evaporate nearly, but not quite, to dryness; now add about half a test-tubeful of *water*, heat, pour the hot liquid into a test-tube, and let it cool.

The nitric acid is destroyed by this treatment:— $\text{HNO}_3 \text{Aq} + (3 + x) \text{HClAq} = 2\text{H}_2\text{O} + \text{NOCl} + 2\text{Cl} + x \text{HClAq}$.

Three cases now present themselves.

- A. A white crystalline pp., which soon settles, forms in the cooling liquid. This pp. is almost certainly PbCl_2 . Proceed as directed under II. A, p. 277.
- B. A white amorphous pp. forms which does not settle quickly. This pp. is almost certainly SbOCl or BiOCl . Proceed as directed under II. B, p. 278.
- C. No pp. forms, even when the liquid is cold. See II. C, p. 278, and proceed as directed there.

NOTE.—If the substance given for analysis is insoluble in water, hydrochloric acid, and *aqua regia*, it must be treated as an

INSOLUBLE SUBSTANCE, and examined by the directions given at the end of this Lesson (p. 285).

EXAMINATION OF THE SOLUTION, FOR METALS

You will now have obtained a solution of the substance under examination.

If the substance did not dissolve in water you will have obtained evidence of the presence or absence of *lead*; and probably also of the presence or absence of *antimony* or *bismuth*.

If the original was a metal, or a mixture of metals, you will have found whether *antimony*, or *tin*, is present or absent.

You must now add the group reagents in order, and examine the pps. produced, by following *carefully* the directions given in preceding Lessons.

For Group I. consult Lesson XLIII., Experiment II., A; p. 245.

For Group II. " " XLIV., " IV., A; p. 258.

For Group III. " " XLV., " III., A; p. 260.

For Group IV. " " XLVI., " II., A; p. 265.

For Group V. " " XLVII., " II., A; p. 270.

For Group VI. " " XLVIII., " II.; p. 274.

The following points must be noted carefully :

(i.) The filtrate from a group pp. is the liquid to which the reagents that precipitate the next group must be added.

(ii.) Every pp. must be washed several times—hot water may generally be used—before its behaviour towards reagents is examined.

The reason for this has been stated; the student should make quite certain he understands the reason.

(iii.) The volume of liquid to which the group reagents for any group are added should not be more than, say, three-quarters of a test-tubeful. If the filtrate from any group pp. amounts to more than this, do not throw away part of it, but concentrate the liquid by evaporation in a basin.

(iv.) As lead, if present, will be found both in Group I. and Group II., when lead has been found in Group I. the pp. in Group II. should be tested not only for lead, but also for one other metal.

When the student has become familiar with the detailed directions given in *Lessons XLIII. to XLVIII.* for obtaining and examining the various group pps. he may find the table intercalated between pp. 282 and 283 useful as a guide.

If this table is to be used successfully a great deal of detail must be supplied by the student himself. The table is to be regarded merely as a general guide to those who have a fair working acquaintance with the methods summarised therein.

SYNOPSIS OF METHODS FOR PREPARING A SOLUTION TO BE EXAMINED FOR METALS

I. Boil a *little* with **water**; if all dissolves add group reagents.

II. If all does not dissolve in water, boil a *little* with **dilute hydrochloric acid**; if all dissolves, add water, boil, and let cool:—

- (i.) If white crystalline pp. forms examine this for PbCl_2 , and filtrate for *Groups II. and onwards*;
- (ii.) If white amorphous pp. forms, warm again; if pp. dissolves, or if it dissolves after adding a *little more* HClAq and warming, it is probably BiOCl or SbOCl ; examine liquid for *Groups II. and onwards*;
- (iii.) If no pp. forms examine liquid for *Groups II. and onwards*.

III. If all does not dissolve in dilute hydrochloric acid, boil a *little* with **conc. hydrochloric acid** for some minutes, add water, boil, and let cool:—

- (i.) If white crystalline pp. forms examine this for PbCl_2 , and filtrate for *Groups II. and onwards*;
- (ii.) If white amorphous pp. forms, warm again; if pp. dissolves, or if it dissolves after adding a *little more* HClAq and warming, it is probably BiOCl or SbOCl ; examine liquid for *Groups II. and onwards*;
- (iii.) If no pp. forms examine liquid for *Groups II. and onwards*.

IV. If all does not dissolve by treatment with conc. hydrochloric acid, boil a *little* with **aqua regia** till most of acid is removed, add water, boil, and let cool :—

(i.) If white solid remains, *wash this thoroughly*, and then examine it for Sb_2O_3 or SnO_2 (p. 280) ; boil down filtrate from white solid nearly to dryness, add a little conc. hydrochloric acid, boil nearly to dryness, add water, boil, and let cool :—

(a) If white crystalline pp. forms examine this for PbCl_2 , and filtrate for *Groups II. and onwards* ;

(β) If white amorphous pp. forms, warm again ; if pp. dissolves, or if it dissolves after adding a *little more* HClAq and warming, it is probably BiOCl or SbOCl ; examine liquid for *Groups II. and onwards* ;

(γ) If no pp. forms examine liquid for *Groups II. and onwards* ;

(ii.) If no solid remains boil nearly to dryness, add a little conc. hydrochloric acid, boil nearly to dryness, add water, boil, and let cool ; examine liquid for *Groups II. and onwards*.

V. If substance is not decomposed by *aqua regia* examine it as an **INSOLUBLE SUBSTANCE** (p. 285).

INSOLUBLE SUBSTANCES

Read the whole of the directions before beginning

The commonest substances that are insoluble in hydrochloric acid, and also in *aqua regia*, are the following: silica and most silicates; certain arsenates; sulphates of barium, strontium, and lead; silver chloride; SnO_2 , Sb_2O_3 , and Sb_2O_5 ; Al_2O_3 , Fe_2O_3 , and Cr_2O_3 , after they have been very strongly heated; carbon and sulphur.

If the appearance of the substance suggests the presence of carbon or sulphur, a special examination should be made for these elements. Carbon is detected by burning a little of the substance in a piece of hard glass tube in a stream of air that has bubbled through potash solution (to remove CO_2), and letting the gaseous products of the burning pass into lime water. Sulphur may be detected by the appearance and smell when a little of the substance is burnt, in a Bunsen flame, on a platinum spatula.

Mix about the quantity of the finely powdered substance indicated in fig. 37 (p. 279) in a capacious porcelain crucible, with five or six times its weight of a mixture of about equal parts dry sodium carbonate and dry potassium carbonate; heat over a Bunsen lamp and then over a foot blowpipe until the whole melts; keep thoroughly molten for about ten minutes, and then allow to cool. Place the crucible in a basin, cover the crucible with water, and boil until the contents of the crucible are thoroughly disintegrated and washed out into the basin; then filter, and wash the residue five or six times with hot water, adding the washings to the filtrate.

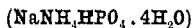
Residue.

Dissolve in as little dilute nitric acid as possible, and evaporate nearly to dryness; add

Solution.

Use about three-fourths for the detection of acids, evaporating to a pasty solid, and

a little *conc. hydrochloric acid*, and again evaporate nearly to dryness; repeat this treatment with *hydrochloric acid*; then add *water*, warm, and filter if there is any insoluble matter. Examine the insoluble portion for *silica* by making a bead of *microcosmic salt*

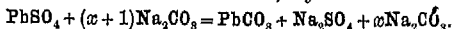


on a piece of *clean* platinum wire, and heating a LITTLE of the substance on this till the bead melts:—If white opaque particles are seen in the melted bead, which particles do not dissolve after some time, a SILICATE is present.¹ Also examine the insoluble matter for Group I. Examine the filtrate from the insoluble portion for the other groups, as far as the end of Group V.

using this as directed in *Lesson LI.* (p. 290). Remember that this substance contains sodium and potassium carbonates.

To the remaining one-fourth of the solution add *dilute hydrochloric acid* until the liquid is slightly acid; evaporate nearly to dryness, add some *water*, warm, and filter if there is any insoluble matter; test the insoluble portion for *silica*,¹ by the *microcosmic bead test*, and examine the filtrate from the insoluble portion for *arsenic*, *antimony*, *tin*, *aluminium*, or *chromium*.

REACTIONS.—Fusion with sodium carbonate decomposes the insoluble salts and oxides, forming, in most cases, a carbonate (or sometimes an oxide) of the metal of the insoluble salt or oxide, and a sodium salt of the acid of the insoluble salt; *e.g.*



The sodium salts thus formed dissolve in water; the carbonates of the metals of the insoluble salts are insoluble in water, but dissolve in dilute nitric acid. If a silicate is present the aqueous solution of the product of fusion contains sodium silicate: but some of the silicate is generally found in the portion insoluble in water. If compounds of arsenic, antimony, tin, aluminium, or chromium are present, the aqueous solution of the product of fusion contains arsenate, antimonate, stannate, aluminate, or chromate of sodium; but compounds of these metals are generally present in that portion of the product of fusion that is insoluble in water.

¹ As fusion in a porcelain crucible may bring silica into the substance, the original substance should also be examined for silica by the *microcosmic bead test*.

LESSON I

REACTIONS OF THE COMMONER ACIDIC RADICLES

Materials required.—Sodium, or potassium, salts of the following acids : boric, carbonic, hydriodic, hydrobromic, hydrochloric, nitric, oxalic, phosphoric, sulphuric, sulphydric, and thiosulphuric.

Group reagents for the acidic radicles have been found only in a few cases. It is necessary almost to deal with each acid by itself, or at any rate to be content with grouping the acids roughly and approximately, and then testing for each member of these rough groups in succession. Happily it is possible, in the cases of fairly simple mixtures of acids, at any rate, to find tests for one acid which are not interfered with by the presence of several other acids.

The grouping adopted in the following directions is based primarily on the reactions of solid salts of the various acids with sulphuric acid. The tests are arranged so that several acidic radicles may be detected in the same mixture of salts.

The directions apply to the detection of the radicles of the following acids only :—

boric, carbonic, hydriodic, hydrobromic, hydrochloric, nitric, oxalic, phosphoric, sulphuric, sulphydric, and thiosulphuric.

GROUP I.—Acids, salts of which react with *dilute sulphuric acid*, either with or without warming, and give off gases recognisable by their properties and reactions :—

carbonic, sulphydric, and thiosulphuric acids.

GROUP II.—Acids, salts of which react with *conc. sulphuric acid*, either with or without warming, and give off gases recognisable by their properties and reactions :—

hydriodic, hydrobromic, hydrochloric, nitric, and oxalic acids.

GROUP III.—Acids, salts of which do not give characteristic reactions with sulphuric acid :—

boric, sulphuric, and phosphoric acids.

Synopsis of those Reactions of the Compounds of certain Acidic Radicles which are Employed in Detecting these Radicles.

The student should perform each of the following reactions with a sodium, or potassium, salt of the acid named. He should make a point of finding out, either from what he has done in Section I. of this book, or from a text-book of descriptive chemistry, what reactions occur in each test which he performs.

GROUP I.—The addition of a little dilute sulphuric acid to

(i.) A solid carbonate causes the evolution of CO_2 , which reacts with lime water to form a white pp. of $CaCO_3$. (See Section I., p. 8.)

(ii.) A sulphide causes the evolution of H_2S , recognised by its smell and the formation of a dark brown pp. of PbS by reacting with solution of a salt of lead. This reaction is more pronounced when heat is used.

A solution of a sulphide gives a black pp. (Ag_2S) with a solution of a salt of silver. This pp. is insoluble in ammonia solution.

(iii.) A thiosulphate, followed by warming, causes the deposition of yellow sulphur, and the evolution of SO_2 ; the gas is recognised by its smell, and the formation of a green solution of chromic sulphate when it reacts with a drop of a solution of potassium chromate placed on filter paper which is held over the mouth of the test-tube.

A solution of a thiosulphate gives a white pp. ($Ag_2S_2O_3$) with a solution of a salt of silver; when the liquid is warmed the pp. is decomposed, until finally black silver sulphide (Ag_2S) is produced.

GROUP II.—The addition of a little conc. sulphuric acid to

(i.) A solid iodide produces some gaseous HI , and generally also a little solid iodine; the gas is recognised by its strongly acid smell, and the solid by its appearance.

Iodides in solution react with an aqueous solution of chlorine

to form chlorides and iodine; iodine dissolves readily in *carbon disulphide* forming a violet liquid which does not mix with, and is heavier than, water.

(ii.) A *solid bromide* produces white, acid-smelling fumes of HBr , mixed with very badly smelling reddish fumes of bromine.

Bromides in solution react with an aqueous solution of *chlorine* to form chlorides and bromine; bromine is soluble in *carbon disulphide* to which it imparts a reddish brown colour.

(iii.) A *solid chloride* produces white, acid-smelling fumes of HCl which form white solid ammonium chloride when brought into contact with *gaseous ammonia*.

Chlorides in solution give a white pp. of silver chloride with solution of a *salt of silver*; this pp. is easily soluble in *ammonia* solution.

(iv.) A *solid nitrate*, followed by heating, causes the evolution of small quantities of the brownish-coloured gas NO_2 .

Nitrates in solution react with *conc. sulphuric acid* and a *cold* solution of *ferrous sulphate* to form various dark brown soluble compounds of ferrous sulphate and nitric oxide ($xFeSO_4.yNO$), which are very easily decomposed by heat. (For details see Section I., p. 70.)

(v.) A *solid oxalate*, followed by heating, produces a mixture of CO and CO_2 ; the former gas is easily ignited and burns with a characteristically coloured, violet-blue flame.

Oxalates in solution give a white pp. of CaC_2O_4 with a solution of a *salt of calcium*; this pp. is soluble in ordinary mineral acids, but is insoluble in *acetic acid*.

GROUP III.—*Solutions of sulphates* give a white pp. of $BaSO_4$ with a solution of a *salt of barium*; this pp. is insoluble in acids.

Solutions of phosphates give a yellow pp. of ammonium phospho-molybdates by warming with nitric acid and *ammonium molybdate* solution.

Solutions of borates are readily decomposed by *hydrochloric acid*, giving some boric acid which remains in the solution and stains *turmeric paper* reddish, especially when the paper is soaked in the liquid and is then dried.

LESSON LI

DETECTION OF THE COMMONER ACIDIC RADICLES

The following directions for detecting certain acidic radicles show how the properties and reactions of compounds of these radicles described in the last lesson are employed for this purpose.

The radicles included in these directions are those of the following acids:—boric, carbonic, hydriodic, hydrobromic, hydrochloric, nitric, oxalic, phosphoric, sulphuric, sulphydric, and thiosulphuric.

The directions do not apply to mixtures of salts some of which seriously modify the reactions of the others; such as a mixture of an iodide and a nitrate; of a bromide and a chloride; of a bromide, a chloride, and an iodide; or of a sulphate, a sulphide, and a thiosulphate.

If the mixture of salts given for analysis is a solid proceed according to part A of these directions.

If the mixture of salts given for analysis is in solution proceed according to part B of these directions (p. 295).

A. THE SUBSTANCE TO BE TESTED IS A SOLID

I. To a small quantity of the solid add about a fourth of a test-tubeful of dilute sulphuric acid:—

(i.) If a colourless, odourless, non-inflammable gas is given off, that produces a turbidity in lime water, this gas is carbon dioxide;

therefore a CARBONATE is present.

(ii.) If a colourless gas is given off, smelling of rotten eggs, and producing a brownish black stain (of lead sulphide) on paper moistened with a solution of a salt of lead and held close to the

mouth of the tube, generally accompanied by the formation of a little very finely divided, white solid, this gas is hydrogen sulphide (the white solid is sulphur);

therefore a **SULPHIDE** is present.

This reaction may not be apparent until heat is applied.

WHETHER A POSITIVE RESULT HAS OR HAS NOT BEEN OBTAINED WITH COLD DILUTE SULPHURIC ACID, WARM THE LIQUID:—

(iii.) If a colourless, non-fuming gas is given off, having the smell of burning sulphur, and changing the colour of *potassium chromate* solution to the green colour of *chromic sulphate* solution when a piece of paper moistened with *one drop* of *potassium chromate* solution is held close to the mouth of the tube; and a very finely divided yellow solid gradually forms in the liquid; the gas is sulphur dioxide, and the solid is sulphur;

therefore a **THIOSULPHATE** is present.

NOTE.—On addition of dilute sulphuric acid effervescence may occur and the smell of hydrogen sulphide may be apparent; this would show a sulphide; but as a carbonate may also be present, the escaping gas must be decanted into lime water.

WHATEVER RESULTS HAVE BEEN OBTAINED UNDER I.,

PROCEED TO II.

II. To a small quantity of the solid add about an eighth of a test-tubeful of concentrated sulphuric acid:—

(i.) If a reddish violet gas is given off, mixed with white, acid-smelling, fumes, the coloured gas is probably iodine, and the white fumes are probably hydrogen iodide; the reaction will be rendered more definite by warming gently (the smell of hydrogen sulphide, and perhaps also of sulphur dioxide, may be apparent on warming; some brownish violet solid [iodine] will be deposited on the cooler parts of the tube);—an *iodide* is probably present.

To confirm the presence of an *iodide* dissolve a little of the original solid in water, or in a very dilute acid—if the solution in water is alkaline add dilute nitric acid till the liquid is slightly acid—add a few drops of *carbon disulphide*, and then

chlorine water until the smell of chlorine is just perceptible, and shake well ; if the carbon disulphide is coloured violet, this colour is caused by iodine dissolved in the carbon disulphide ;

therefore an IODINE is present.

(ii.) If a brownish red, very badly smelling gas is given off, accompanied by white, acid-smelling fumes, the coloured gas is probably bromine, and the white fumes are probably hydrogen bromide ; *the reaction will be rendered more definite by warming gently ;—a bromide is probably present.*

To confirm the presence of a bromide, dissolve a little of the original solid in water, or in a little very dilute acid—if the solution in water is alkaline add dilute nitric acid till the liquid is slightly acid—add a few drops of carbon disulphide, and then chlorine water until the smell of chlorine is just perceptible, and shake well ; if the carbon disulphide is coloured reddish brown, this colour is caused by bromine dissolved in the carbon disulphide ;

therefore a BROMIDE is present.

(iii.) If a strongly-fuming, acid-smelling, white vapour is given off, this vapour is probably hydrogen chloride ;—*a chloride is probably present. The reaction will be rendered more definite by warming gently.*

To confirm the presence of a chloride, dissolve a little of the original solid in water (or in dilute nitric acid), add a slight excess of nitric acid, and then silver nitrate solution, collect the pp. that forms on a filter, wash it a few times, remove the filtrate and washings, put a clean tube beneath the funnel containing the pp., pour warm ammonia over the pp., and add a slight excess of nitric acid to the ammoniacal solution that runs through the filter into the tube ; if a white pp. is produced, this pp. is silver chloride—which is soluble in ammonia but not in dilute nitric acid ;

therefore a CHLORIDE is present.

NOTE.—Always perform the silver nitrate test for a chloride whether warming with conc. sulphuric acid has or has not indicated the presence of a chloride.

NOTE REGARDING THE SILVER NITRATE TEST FOR A CHLORIDE

If a sulphide is present, along with a chloride, the pp. by AgNO_3Aq will be black, because black Ag_2S will be pp-d. along with white AgCl ; but ammonia will dissolve only AgCl from this pp., and on adding HNO_3Aq to the solution in ammonia white AgCl will be re-precipitated.

If a thiosulphate is present, along with a chloride, the pp. by AgNO_3Aq will be white, but it will rapidly become grey, then brown, and finally black, because white $\text{Ag}_2\text{S}_2\text{O}_3$ soon decomposes to black Ag_2S ; but ammonia will dissolve only AgCl from this pp., and on adding HNO_3Aq to the solution in ammonia white AgCl will be re-precipitated.

WHETHER A POSITIVE RESULT HAS OR HAS NOT BEEN OBTAINED WITH COLD CONC. SULPHURIC ACID, WARM A LITTLE OF THE ORIGINAL SUBSTANCE WITH A SMALL QUANTITY OF THIS ACID :—

(iv.) If an acid-smelling gas, with a slightly brownish red colour, is given off on warming with conc. sulphuric acid, this gas is probably nitrogen dioxide, and therefore a nitrate is probably present.

To confirm the presence of a nitrate, THOROUGHLY COOL the contents of the tube in which the original solid has been heated with conc. sulphuric acid, then hold the tube in a sloping position, and slowly pour into it a solution of ferrous sulphate freshly prepared in COLD WATER; if a blackish brown colour is produced, where the lighter ferrous sulphate solution meets the heavier liquid containing sulphuric acid, this colour is caused by a compound, or compounds, of NO and FeSO_4 dissolved in the water ($x\text{FeSO}_4.y\text{NO}$);

therefore a NITRATE is present.

NOTE.—Always perform the ferrous sulphate test for a nitrate whether heating with conc. sulphuric acid has or has not indicated the presence of a nitrate.

(v.) If a colourless, non-fuming gas is given off on warming with conc. sulphuric acid, which gas takes fire, and burns with a pale bluish lavender flame when a light is brought to the

mouth of the tube, this gas is carbon monoxide, and *probably an oxalate is present.*

To confirm the presence of an oxalate, dissolve a little of the original solid in water, add acetic acid in excess, and then calcium chloride solution; if a white pp. is produced, this pp. is calcium oxalate;

therefore an OXALATE is present.

NOTE REGARDING THE CONFIRMATORY TEST² FOR AN OXALATE

If the original is not soluble in water dissolve it in dilute hydrochloric or nitric acid, add a slight excess of ammonia, then excess of acetic acid, and then calcium chloride solution:— calcium oxalate is soluble in the ordinary mineral acids, but is insoluble in acetic acid.

NOTE.—Perform the calcium chloride test for an oxalate even if heating with conc. sulphuric acid has not indicated the presence of an oxalate.

WHATEVER RESULTS HAVE BEEN OBTAINED UNDER I.

AND II., PROCEED TO III.

III. Dissolve some of the original solid in water, or dilute nitric acid, and divide the solution into two parts:—

(i.) To one portion of the solution add barium nitrate solution; a white pp. that does not dissolve in dilute nitric acid, nor in dilute hydrochloric acid, is barium sulphate;

therefore a SULPHATE is present.

(ii.) To the other portion of the solution add dilute nitric acid, heat nearly to boiling, and then add ammonium molybdate solution; if a light yellow pp. forms slowly this pp. is an ammonium phosphomolybdate;

therefore a PHOSPHATE is present.

NOTE REGARDING THE TEST FOR A PHOSPHATE

If the original solution contains a thiosulphate, warming with nitric acid will cause the separation of yellow, finely divided sulphur, but the pp. by ammonium molybdate will, nevertheless, be quite apparent.

This test for a phosphate supposes the absence of arsenic.

WHATEVER RESULTS HAVE BEEN OBTAINED UNDER I.,
II., AND III., PROCEED TO IV.

IV. Dissolve a little of the original solid in dilute hydrochloric acid:—

Immerse a piece of *turneric paper* in the solution, soak the paper for some time, in the liquid, then remove it, and dry it thoroughly by holding it at the side of a Bunsen flame; if the paper appears reddish when dry, this colour is caused by boric acid;

∴ therefore a BORATE is present.

B. THE SUBSTANCE TO BE TESTED IS A SOLUTION.

WHATEVER RESULTS ARE OBTAINED IN I., PROCEED TO II.
AND III.

I. Addition of dilute sulphuric acid will give the reactions for a carbonate, a sulphide, and a thiosulphate [see A. I. (i.), (ii.), (iii.)].

II. Heating with conc. sulphuric acid may give indications of an iodide, a bromide, and a nitrate [see A. II. (i.), (ii.), and (iv.)].

III. Test separate portions of the solution;

(i.) For an iodide, by the carbon disulphide test [see A. II. (i.), p. 291].

(ii.) For a bromide, by the carbon disulphide test [see A. II. (ii.), p. 292].

(iii.) For a chloride, by the silver nitrate test [see A. II. (iii.), p. 292].

(iv.) For a nitrate, by the ferrous sulphate test [see A. II. (iv.), p. 293].

(v.) For an oxalate, by the calcium chloride test [see A. II. (v.), p. 294].

(vi.) For a sulphate, by the barium nitrate test [see A. III. (i.), p. 294].

(vii.) For a phosphate, by the ammonium molybdate test [see A. III. (ii.), p. 294].

(viii.) For a borate, by the turmeric-paper test [see A. IV. above].

When the student has become familiar with the detailed directions given in *this Lesson* for detecting the various acidic radicles he may find the following table useful as a guide.

If this table is to be used successfully a great deal of detail must be supplied by the student himself. The table is to be regarded merely as a general guide to those who have a fair working acquaintance with the methods summarised therein.

SYNOPSIS OF TESTS FOR ACIDIC RADICLES

(The references are to the pages where details of the tests will be found)

GROUP I.—To the solid add dil. $\text{H}_2\text{SO}_4\text{Aq}$ and notice what occurs; then warm:—			
CO_2 is given off (confirm by CaOAq).	H_2S is given off (confirm by lead paper).	SO_2 is given off, on warming, and S is deposited.	
p. 290. CARBONATE.	p. 290. SULPHIDE.	p. 291 THIOSULPHATE.	
GROUP II.—To the solid add conc. H_2SO_4 , and notice what occurs; then warm:—			
I and HI are given off (more apparent on warming).	HCl is given off (more apparent on warming).	NO_2 is given off on heating.	CO is given off on heating.
Confirm by CS_2 test.	Confirm by AgNO_3Aq test, p. 292.	Confirm by FeSO_4Aq test, p. 293.	Confirm by CaCl_2Aq test, p. 294.
p. 291.	p. 292.		
GROUP III.—Dissolve the solid in water, or in dil. HNO_3Aq , and test separate portions of this solution:—			
$\text{Ba}(\text{NO}_3)_2\text{Aq}$ gives white pp. (BaSO ₄) insol. dil HClAq .	After adding HNO_3Aq and heating, ammonium molybdate gives yellow pp.	GROUP IV.—Dissolve the solid in dil. HClAq ; soak turmeric paper in this solution, and dry it.	
p. 294. SULPHATE.	p. 294. PHOSPHATE.	If paper is turned reddish, this is caused by boric acid.	
		p. 295. BORATE.	

NOTE.—If substance is a solution the only acidic radicles which will be indicated by the use of sulphuric acid are those of carbonic, sulphuric, and thiosulphuric acids, indications may also be given of the radicles of hydriodic, hydrobromic, and nitric acids, but these, and the other acidic radicles, must be tested for in separate portions of the solution by the confirmatory tests referred to above.

BEFORE BEGINNING THE ANALYSIS OF A MIXTURE OF METALS,
OR OF SALTS, READ THE FOLLOWING GENERAL NOTE.

Note regarding the qualitative analysis of mixtures, of the commoner metals, and of mixtures of salts, when not more than one metal is present in any one group, and when the reactions of any one acidic radicle are not seriously modified by the other acidic radicles which are present.

I. Proceed to the detection of the metals, in accordance with the directions given in *Lesson XLIX.* (pp. 276 to 283).

II. Detect the acidic radicles, in accordance with the directions given in *Lesson LI.* (pp. 290 to 297).

NOTE.—When the analyst is dealing with mixtures that may contain several metals in each group, and many acidic radicles, it is advisable to remove the metals, and to combine the acidic radicles with sodium (by boiling the original substance with sodium carbonate), before testing for the acidic radicles; but this procedure is not necessary in such comparatively simple cases as those now under consideration.

LESSON LII

EXAMINATION OF A SOLID BY DRY TESTS

WHATEVER RESULTS ARE OBTAINED IN I., PROCEED TO II.-VI.

I. Heat a *very little* in a *dry* narrow tube of hard glass.

A. A sublimate is formed:—

- (i.) Reddish drops sulphur.
- (ii.) White ammonium salts, As_2O_3 ,
 Sb_2O_3 , HgCl_2 , or HgCl_2 .
- (iii.) Shining, mirror-like arsenic.
- (iv.) Metallic globules mercury.

B. A gas is given off:—

- (i.) Brown-red = NO_2 nitrates.
- (ii.) Colourless, smelling of NH_3 . ammonium salts.
- (iii.) „ „ „ SO_2 . sulphites.

II. Take a *very little* on a bead of borax and heat, till thoroughly melted, in the outer, upper part of a Bunsen flame. Notice colour of bead *both when hot and cold*:—

- (i.) Yellow-red (pale greenish when cold) compounds of iron.
- (ii.) Green (blue-green when cold) „ copper.
- (iii.) Blue (hot and cold) „ cobalt.
- (iv.) Emerald-green (hot and cold) „ chromium.
- (v.) Amethyst (nearly colourless when heated for some time in luminous tip of Bunsen flame) „ manganese.
- (vi.) Pinkish brown „ „ nickel.

Silver compounds produce a grey, opaque bead.

III. Take a *very little* on a *clean* platinum wire (that is, a wire which does not colour a hot non-luminous flame) and bring it into the lower, outer part of a Bunsen flame. Notice colour imparted to the flame; if there is no distinct colouration, moisten the substance on the wire with *conc. hydrochloric acid* and bring it again into the flame:—

- (i.) Deep yellow compounds of sodium.
- (ii.) Violet-lavender (looks purple-violet through a *thick piece* of blue glass) „ „ potassium.

NOTE.—A blue-violet colour, generally accompanied by white fumes, is given by compounds of antimony, arsenic, bismuth, lead, and various other heavy metals.

- (iii.) Grass-green compounds of barium.
- (iv.) Crimson to red „ strontium or calcium.
- (v.) Blue-green „ copper.

IV. Mix a *little* with three or four times as much solid *dry sodium carbonate* and a little solid *potassium cyanide*.

NOTE.—POTASSIUM CYANIDE IS EXTREMELY POISONOUS.

Place the mixture in a *small* hole in a piece of charcoal, heat in *reducing flame* of a blowpipe till melted, scrape the melted mass and some of the charcoal around it into a mortar, grind with water, and pour off water and light particles; repeat washing till only small metal-like particles, or a heavy dark powder, remain in the mortar. Rub these particles, or powder, with a pestle and notice whether the solid flattens out or breaks into powder:—

- (i.) Particles are reddish and malleable copper.
- (ii.) Particles are grey and malleable lead, silver, or perhaps tin.

Lead gives a yellow incrustation on the charcoal; tin, a very slight incrustation which is yellow when hot; and silver, no incrustation. (These incrustations are oxides of the metals.)

(iii.) Particles are grey and brittle . . antimony or bismuth.
Antimony gives a white, and bismuth a yellow-orange, incrustation.

(iv.) A blackish, *magnetic* powder is
produced¹ iron, cobalt, or nickel.

V. Mix a *little* with three or four times as much solid *dry sodium carbonate*, heat on charcoal in *reducing flame* of blowpipe till melted, scrape the melted mass on to a silver coin, and moisten with water.

If the silver is stained brown this shows that original contained a compound of sulphur.

NOTE.—Compounds of sulphur are reduced by this treatment, and Na_2S is formed; this dissolves in water and the solution in contact with silver forms a slight pp. of Ag_2S .

VI. Heat a *little*, supported on a small loop on the end of a piece of platinum wire, in a Bunsen flame for a few minutes; then moisten with three or four drops (not more) of a solution of *cobalt nitrate*, and heat again to *full redness for some minutes*; then allow to cool:—

(i.) Residue is coloured blue . . compounds of aluminium
(certain phosphates also
give this reaction).

(ii.) Residue is coloured green . . compounds of zinc.

¹ To try whether the powder is magnetic, wash some of it on to a piece of broken glass, pour off the water, heat the powder over a *very low flame* till quite dry, and then bring a magnetised knife-blade close to the dry powder.

APPENDIX I

MAKING APPARATUS

Cutting glass tubes.—Make a clean scratch with a sharp three-edged file across the tube; hold the tube with the scratch upwards, and pull the two ends apart with a slightly downward inclination; if the tube is wide, a deep mark, extending nearly round the tube, should be made. Or a smaller scratch may be made, and the red-hot tip of a piece of glass tube, *drawn to a fine point*, may be brought on to the scratch; if the crack thus made does not pass quite round the tube, the small red-hot tip of the piece of glass tubing may be brought on to the tube near one end of the crack and then moved slowly round the tube, when the crack will follow the moving piece of hot glass. The edges of the ends of a glass tube should always be melted slightly, by holding each end in a hot flame, before the tube is used.

Bending glass tubes.—Use an ordinary fish-tail burner the flame of which is about two inches broad. Hold the glass tube in the broadest part of the flame, and keep it in constant rotation until the glass has softened; then remove the tube from the flame and bend it *very slowly*.

Drawing out glass tubes.—Heat the glass tube, rotating it constantly, in a blowpipe flame of such a size that a length of the tube at least equal to the diameter of the tube is softened; continue to heat, with constant rotation, but without drawing the ends apart, until the walls of the tube are thickened somewhat at the softened part; then remove the tube from the flame, and *very slowly* draw the ends apart until the tube is narrowed sufficiently. Let the tube cool, cut it at the proper place, and round the edges of both ends by holding them in a Bunsen flame for a moment or two.

Closing the ends of glass tubes.—Proceed as directed under *drawing out glass tubes* until the glass softens, then *slowly* draw the ends a *very little way* apart; keep the narrowed part sufficiently hot to allow

the walls of the tube at this part to thicken; then heat a little more strongly and *slowly* draw the ends quite apart; now remove the little knob of glass from the closed end of the tube by applying a *very small* blowpipe flame to it and drawing off the melted knob by means of a piece of pointed glass tubing. Now heat the closed end of the tube till it softens, rotating the tube constantly; remove the tube from the flame and blow into it *very gently* so as to cause the melted end to become semicircular.

Boring holes in corks, and fitting glass tubes into corks.—Choose a cork rather larger than the opening into which it is to be fitted; wrap the cork in a piece of paper, and roll it under the foot, pressing gently and equally while you do this.

If a hole is to be bored in a softened cork with a file, place the cork on the table and gently press a *little way* into it the pointed end of a rat-tail file; then repeat this process at the other end of the cork, taking care that the two holes are exactly opposite one another. By repeating these processes the holes will meet; now hold the cork lengthwise on the table, and work the file into the hole you have made, with a gentle rotatory motion until the hole in the cork is nearly, but not quite, as wide as the diameter of the tube that is to be fitted into it.

Cork borers are very useful for making holes in corks, and they are manipulated more easily than a file.

When fitting a glass tube into a hole in a cork, grasp the tube near the end that is to be inserted into the cork, wet this end of the tube, and work it into the hole in the cork *gradually*, with a *gentle* rotatory motion. *The rough edges of the ends of glass tubes must always be melted smooth before the tubes are fitted into corks.*

APPENDIX II

TABLES

I. TABLE OF SOLUBILITIES

THE table on the following page is so arranged that the *bases* are placed at the heads of the columns, and the *acidic radicles* with which the bases may be combined are placed at the side.

The figures refer to the various *menstrua* in which the salts are soluble. Thus:

I. means soluble in water.

II. means soluble in acids, but insoluble in water.

III. means insoluble in both water and acids.

The solubilities of the more commonly occurring salts are indicated by Roman figures—I., II., III., while those salts which are of less frequent occurrence have Arabic figures placed after them—1, 2, or 3.

Some substances are placed in more than one class. This is indicated thus: 1-2 means a substance very slightly soluble in water, but soluble in acids; 1-3 means a substance soluble with difficulty in water, the solubility of which is not increased by the addition of acids; 2-3 means a substance insoluble in water, and but slightly soluble in acids.

II. TABLE SHOWING THE RELATION BETWEEN ENGLISH WEIGHTS
AND MEASURES AND THOSE OF THE METRIC SYSTEM

<i>Measures of Weight</i>	
Milligram	= .01543235 troy grain.
Centigram	= .1543235 " "
Decigram	= 1.543235 " "
Gram	= 15.43235 " grains.
"	= .648 pennyweight.
"	= .03216 oz. avoirdupois.
"	= .03527 oz. troy.
Kilogram	= 2.6803 lbs. troy.
"	= 2.20462 lbs. avoirdupois.
Metric Ton (1000 kilos.)	= 2204.62 " " "

Measures of Length

Millimetre	=	·08937 inch.
Centimetre	=	·8937 "
Decimetre	=	8·937 inches
Metre	=	39·37 "
"	=	3·2809 feet.
"	=	1·0937 yard.

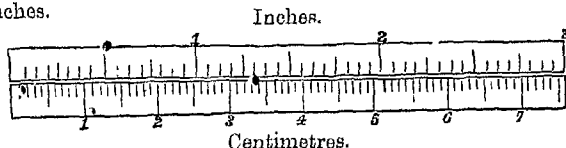
Inch = 2·53995 centimetres. Foot = 3·04794 decimetres. Yard = 91·438 centimetres. Mile = 1609·32 metres.

The following *approximate* relations may be found useful:—

1 gram	=	15½ grains	28½ grams	=	1 oz.
5 grams	=	77½ "	100 "	=	3½ oz.
10 "	=	155 "	142 "	=	5 oz.
20 "	=	310 "	284 "	=	10 oz.
10 c.c.	=	½ fluid oz.	210 c.c.	=	7 fluid oz.
80 c.c.	=	1 "	270 c.c.	=	9 "
50 c.c.	=	1½ "	300 c.c.	=	10 "
60 c.c.	=	2 "	360 c.c.	=	12 "
90 c.c.	=	3 "	420 c.c.	=	14 "
100 c.c.	=	3½ "	450 c.c.	=	15 "
200 c.c.	=	6½ "	500 c.c.	=	nearly 17 oz.

¼ litre = 22 gallon; 4½ litres = nearly 1 gallon. A Winchester quart bottle contains about 2½ litres of water.

The accompanying scale shows the relation between centimetres and inches.



III. TO CONVERT DEGREES FAHRENHEIT INTO DEGREES CENTIGRADE AND VICE VERSA

$$(C.^{\circ} \times 1.8) + 32 = F.^{\circ}$$

$$(F.^{\circ} - 32) \div 1.8 = C.^{\circ}$$

IV. TO CONVERT DEGREES OF TWADDELL'S HYDROMETER INTO SPECIFIC GRAVITY

$$(\text{Degrees Twaddell} \times 5) + 1000 = \text{sp. gravity.}$$

$$(\text{Sp. Gravity} - 1000) \div 5 = \text{degrees Twaddell.}$$

1 An ordinary test-tube holds about 80 c.c. of water.

V. NAMES, SYMBOLS, AND APPROXIMATE ATOMIC WEIGHTS
OF THE ELEMENTS

The Atomic Weights are given in round numbers

Name.	Symbol.	Approx. atomic weight.	Name.	Symbol.	Approx. atomic weight.
Aluminium	Al	27	Nickel	Ni	58.5
Antimony	Sb	120	Niobium	Nb	94
Arsenic	As	75	Nitrogen	N	14
Barium	Ba	137	Osmium	Os	191
Beryllium	Be	9	Oxygen	O	16
Bismuth	Bi	208	Palladium	Pd	106
Boron	B	11	Phosphorus	P	31
Bromine	Br	80	Platinum	Pt	194
Cadmium	Cd	112	Potassium	K	39
Cæsium	Cs	133	Rhodium	Rh	103
Calcium	Ca	40	Rubidium	Rb	85.5
Carbon	C	12	Ruthenium	Ru	101
Cerium	Ce	140	Scandium	Sc	44
Chlorine	Cl	35.5	Selenium	Se	79
Chromium	Cr	52	Silicon	Si	28
Cobalt	Co	59	Silver	Ag	108
Copper	Cu	63	Sodium	Na	23
Fluorine	F	19	Strontium	Sr	87
Gallium	Ga	70	Sulphur	S	32
Germanium	Ge	72	Tantalum	Ta	182
Gold	Au	197	Tellurium	Te	125(2)
Hydrogen	H	1	Thallium	Tl	204
Indium	In	113	Thorium	Th	232
Iodine	I	127	Tin	Sn	118
Iridium	Ir	192	Titanium	Ti	48
Iron	Fe	56	Tungsten	W	184
Lanthanum	La	139	Uranium	U	240
Lead	Pb	207	Vanadium	V	51
Lithium	Li	7	Ytterbium	Yb	173
Magnesium	Mg	24	Yttrium	Y	89
Manganese	Mn	55	Zinc	Zn	65
Mercury	Hg	200	Zirconium	Zr	90
Molybdenum	Mo	96			

APPENDIX III

REAGENTS

Name.	Formula.	Directions for making a Solution for Laboratory Use.
Hydrochloric acid	HCl	Mix 1 part of conc. acid with 8 parts of water.
Ammonia	NH ₃	Mix 1 part of conc. solution with 8 parts of water.
Acetic acid	H ₃ C ₂ O ₂	Mix 1 part of conc. acid solution with 2 parts of water.
Ammonium sulphide	(NH ₄) ₂ S	Mix 1 part of conc. solution with 1 part of water.
Sulphuric acid	H ₂ SO ₄	To 8 or 10 parts water add <i>slowly</i> 1 part conc. acid.
Nitric acid	HNO ₃	Mix 1 part conc. acid with 8 parts water.
Potash	KOH	Dissolve 1 part by weight in 6 or 8 parts water by measure.
Soda	NaOH	Dissolve 1 part by weight in 6 or 8 parts water by measure.
Ammonium carbonate	(NH ₄) ₂ CO ₃	Dissolve 1 part by weight in 5 or 6 parts water by measure.
Ammonium oxalate	(NH ₄) ₂ C ₂ O ₄ · 2H ₂ O	Dissolve 1 part by weight in 15 or 20 parts water by measure.
Barium nitrate	Ba(NO ₃) ₂	Dissolve 1 part by weight in about 50 parts water by measure.
Cobalt nitrate	Co(NO ₃) ₂ · 6H ₂ O	Dissolve 1 part by weight in about 50 parts water by measure.

Name.	Formula.	Directions for making a Solution for Laboratory Use.
Ferric chloride	FeCl_3	Dissolve 1 part by weight in about 50 parts water by measure.
Potassium iodide	KI	Dissolve 1 part by weight in about 50 parts water by measure.
Potassium ferro-cyanide	$\text{K}_4\text{Fe}(\text{CN})_6$	Dissolve 1 part by weight in about 50 parts water by measure.
Silver nitrate	AgNO_3	Dissolve 1 part by weight in about 100 parts water by measure.
Copper sulphate	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	Dissolve 1 part by weight in about 100 parts water by measure.
Potassium sulpho-cyanide	KCNS	Dissolve 1 part by weight in about 100 parts water by measure.
Stannouschloride	$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$	Dissolve 1 part by weight in about 100 parts water by measure, containing a little hydrochloric acid.

Other ordinary reagents.—Dissolve 1 part of each in from 12 to 15 parts of water by measure.

To make lime water.—Shake slaked lime with distilled water in a Winchester quart for about 10 or 15 minutes and allow to settle.

Silver Residues.—Add hydrochloric acid; collect solid on a large filter, and wash repeatedly with hot water. Then boil with a little dilute nitric acid, and again wash repeatedly with hot water. Press solid matter in calico; mix it with its own weight of powdered borax and three times its weight of dry sodium carbonate; place mixture in earthenware crucible and heat in a good furnace till melted. Remove crucible and tap it to cause silver to gather to a lump; allow to cool; break the crucible, and remove the lump of silver. Boil with water; then dissolve in the smallest possible quantity of dilute nitric acid; evaporate to the crystallising point and let cool—evaporate mother liquor a little further to get second crop of crystals. Drain crystals of silver nitrate; press them in paper, and recrystallise several times from water.

Platinum Residues.—Evaporate all to dryness; boil with water; pour off water; add concentrated solution of oxalic acid and evaporate to dryness. Heat in a good furnace, using an earthenware crucible, till quite black. Boil the platinum with conc. hydrochloric acid for some time; wash with hot water *till washings are quite neutral to litmus*; then boil with nitric acid. Pour off nitric acid, and wash repeatedly with hot water. Now dissolve in 1 part conc. nitric acid mixed with 8 parts conc. hydrochloric acid, by heating in a basin; evaporate to dryness at 100°; add a little conc. hydrochloric acid and evaporate again to complete dryness at 100°; repeat the evaporation to complete dryness at 100° with conc. hydrochloric acid. Then heat at 100° till every trace of hydrochloric acid is removed.